



# CHEMICAL ABSTRACTS

Vol. 16.

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No. 15

## 1—APPARATUS

C. G. DERRICK

Report on standardization of sizes and shapes of apparatus. I. W. D. COLLINS. *J. Ind. Eng. Chem.* 13, 1070-4(1921); II. *Ibid* 14, 654-9, 738-42. E. J. C.

A microextraction apparatus. F. LAQUER. *Z. physiol. Chem.* 118, 215-7(1922).—The app. used by L. in the detn. of lactic acid (*C. A.* 16, 2545) is shown. The essential part amts. to a test-tube with a side arm somewhat below the middle point directed downward at a slight angle. In the test-tube is a funnel with stem reaching to the bottom through which the condensed ether passes to the bottom of the material being extd. The side arm serves for the entrance of ether vapor as well as for the return of the lactic acid-contg. ether. The remainder of the app. consists of a flask attached to the side arm and a condenser to the end of the test-tub.

R. L. STEHLE

Oven for microelementary analysis, with tube burners. E. DIEPOLDER. *Chem.-Ztg.* 46, 455(1922).—The new feature of this oven is a tube burner which is used to heat the part of the combustion tube contg. the boats. This burner has a number of openings 7 mm. apart, arranged in a zigzag line, and the flames issuing from the openings may be individually regulated by means of small rods. Thus the heating may be regulated and localized at will.

C. C. VAN VOORHIS

Determination of solubility. G. W. WALKER. *Chem. News* 124, 256(1922).—W. explains by aid of a rough drawing a simple app. for detg. the soly. of solids in liquids.

E. G. R. ARDACH

Simple bubbling hydrogen electrode. J. R. HAAG. *Science* 55, 460-1(1922).—An electrode vessel whose chief advantage depends upon the use of a small amt. of soln.

C. R. PARK

The boiling-point test for liquids. F. WILBUR SHULENBERGER. *Paint, Oil and Chem. Rev.* 73, No. 24, 10-11(1922).—Description of various devices for detg. b. ps.

F. A. WERTZ

An apparatus for handling deliquescent crystals. C. B. SLAWSON. *Am. Mineral.* 7, 25-6(1922).—The crystals are handled in a galvanized-Fe box with glass windows at top and front, the arms of the operator entering through rubber sleeves at either end.

E. T. WHERRY

Two machines for rapidly weighing loads of a few milligrams. RESEARCH STAFF OF THE GENERAL ELECTRIC CO., LTD., London (E. M. AND C. G. EDEN). *J. Sci. Instruments* Prelim. No. 1922, 15-21.—The two machines described were designed for sorting elec.-lamp filaments to an accuracy within 5% of their wt. A cantilever spring is used in the first machine and the motion of its end is magnified by optical projection 30 times. The scale (0 to 40 mg.) is 13 cm. long. The second machine consists of a small weighing beam controlled by a hair spring. Mechanical magnification between 10 and 100 times is obtained by a fine wire tension lever connecting to a wire hanging in a catenary under its own wt. The movement of the catenary wire is magnified optically 30 to 50 times. Curves showing sensitivity of balance, and effect of stiffness of controlling spring and catenary are given. The speed of each balance is about 400 filaments per hr.

D. E. S.

**Thermoregulator.** E. B. STARKY and N. E. GORDON. *J. Ind. Eng. Chem.* 14, 541(1922).—The instrument is actuated by the expansion and contraction of toluene. The regulator tube connects to a U-tube with contact wires in which mercury is placed. An ingenious device makes the filling and regulation easy. No relay is required and no trouble is had with corrosion of contacts. Accuracy is 0.05°. D. E. S.

**Laboratory sodium press.** ERNST BECKMANN. *Ber.* 55, 766-8(1922).—The press consists of a spindle, moved vertically by a worm, and a capsule into which the spindle enters. The Na is forced through a hole 1 mm. in diam. at the bottom of the capsule. The capsule holds 46 g. The spindle carries a graduated disk; the proportions are such that one complete turn of the spindle delivers 3.7 g. Na. T. S. CARSWELL

**Union gas calorimeter.** AXEL DANIELSON. *Teknisk. Tidskrift* 52, 343-4(1922).—A modification of Strach's calorimeter, designed by O. Dommer, Karlsruhe, was tried out in a Stockholm gas plant. It is a very serviceable instrument. It gave calorific values which averaged 2% less than the Junker calorimeter. A. R. ROSE

**Total-radiation pyrometer.** EBERHARD ZOFF. *Z. Ver. deut. Ing.* 65, 1267(1921).—Brief description of the Siemens and Halske so-called Ardrometer. W. P. WHITE

**Apparatus of transparent bakelite for measuring hydrofluoric acid.** L. J. CURTMAN. *J. Ind. Eng. Chem.* 14, 610(1922).—The advantages of graduates and "medicine" droppers (described) are outlined. E. J. C.

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Diffusions of solutions (Littlewood) 2.

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**Vaporizer for liquefied gases.** E. S. ANDREWS. U. S. 1,417,292, May 23. The app. is adapted for use with liquid O or N.

**Apparatus for sterilizing material in open vessels.** F. H. LANDRUM and A. N. CRAMER. U. S. 1,417,182, May 23.

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## 2—GENERAL AND PHYSICAL CHEMISTRY

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W. E. HENDERSON AND EDWARD MACK

**A new study in alchemy.** C. C. BELL. *Chemist and Druggist* 94, 877-83(1921).—A survey of alchemy, with illustrations and notes. S. WALDBOTT

**Determination of the atomic weight of tellurium.** P. BRUYLANTS and G. DESMET. *Bull. soc. chim. Belg.* 28, 264-6(1919).—The starting material was pure Te prepd. from  $H_2Te$ . The Te was dissolved in  $HNO_3$  and the soln. evapd. to dryness, the residue being calcined and melted. The  $TeO_2$  was dissolved in pure aq. NaOH and the Te estd. volumetrically either in alk. or just acid soln. by the method of Marckwald and Folzik (*C. A.* 4, 2244). The mean of 12 estns. in alk. soln. gave the value 127.8 for the at. wt., and of 9 estns. in acid soln. the value 127.65. J. C. S.

**The crystal structure of magnesium oxide.** W. GERLACH and O. PAULI. *Z. Physik.* 7, 116-23(1921).—X-ray photographs of  $MgO$  from various sources show it to form a face-centered cubic lattice of the NaCl type. The edge of the elementary cube is  $4.20 \times 10^{-8}$  cm. The crystal lattice consists of bivalent ions. A. E. SYEARN

**Röntgenographic determination of crystal arrangement.** M. POLANYI. *Naturwissenschaften* 10, 411-6(1922).—Röntgenographic methods must be employed to det. whether a crystal lattice is changed by elongation of a single crystal. By means of a filament diagram it was found that for a Zn crystal (1) the lattice changes its orientation with respect to the longitudinal axis when elongated; (2) in the section drawn out to a flat band (cf. Schiebold, *Z. Physik* 9, 180(1922); Carpenter and Elam, *C. A.* 16, 1728; Gomperz, *C. A.* 16, 1387) the angle that the hexagonal axis of the crystal lattice makes with the longitudinal axis changes from  $10^\circ$  to  $18^\circ$  and (3) the cylindrical fila-

ments resulting from further elongation of the flat bands have the same orientation of their lattices as the flat bands. It is maintained that this same kind of shift in the orientation of the lattice occurs in a Zn wire as in the individual crystal. A bibliography is appended.

C. C. DAVIS

**The crystalline characters of calcium carbide.** C. H. WARREN. *Am. J. Sci.* 2, 120-8(1921).—CaC<sub>2</sub> made in the elec. furnace is usually a granular or columnar crystal aggregate. The cleavage is pseudo-cubic in character and the twinning is polysynthetic. Its color is purplish or lilac-yellow in transmitted light except when in very thin sections which appear almost colorless. The transparency is good in thin sections.  $n$  is 1.75 and the double refraction is strong, being at least 0.050. In general the extinction is parallel to the rectangular cleavages. Interference figures have been observed in which one arm of the cross is heavier than the other. The crystal system has not been definitely established but is either tetragonal or orthorhombic. The slow decompn. of CaC<sub>2</sub> by water has been examd. microscopically and appears to involve the passage of one cryst. substance to another without the immediate breaking down of the essential crystal substance. The cryst. and optical properties of calcium cyanamide are also given.

W. G. FRANCE

**The crystal structures of the alkali halides.** II. EUGEN POSNJAK AND R. W. G. WYCKOFF. *J. Wash. Acad. Sci.* 12, 248-51(1922); cf. *C. A.* 16, 528.—The following salts have the "sodium chloride arrangement" of their atoms: LiCl,  $d_{100} = 5.17 \text{ \AA.}$ ; LiBr,  $d_{100} = 5.48 \text{ \AA.}$ ; LiI,  $d_{100} = 6.06 \text{ \AA.}$ ; NaF,  $d_{100} = 4.81 \text{ \AA.}$ ; KF,  $d_{100} = 5.36 \text{ \AA.}$ ; CsF,  $d_{100} = 6.03 \text{ \AA.}$  By  $d_{100}$  is meant the length of the side of the unit cube. The diffraction data obtained from RbF were such as to indicate that additional work was necessary to obtain its structure in a satisfactory fashion. A tabulation of the structures of all of the alkali halides is appended.

RALPH W. G. WYCKOFF

**The crystal structures of the hexammoniates of the nickel halides.** R. W. G. WYCKOFF. *J. Am. Chem. Soc.* 44, 1239-45(1922).—By methods based upon the results of the theory of space groups and taking the data from Laue photographs and reflection spectra, it is shown that these salts have the same structure as NH<sub>4</sub> chloroplatinate (*C. A.* 16, 1037) with Ni atoms replacing the Pt atoms, halogen atoms the NH<sub>4</sub> groups and NH<sub>4</sub> groups the Cl atoms. The length of the side of the unit cube for NiCl<sub>2</sub>·6NH<sub>3</sub> is 10.09  $\text{\AA.}$ ; for the corresponding bromide and iodide it is 10.48  $\text{\AA.}$  and 11.01  $\text{\AA.}$

RALPH W. G. WYCKOFF

**The composition and crystal structure of nickel nitrate hexammoniate.** R. W. G. WYCKOFF. *J. Am. Chem. Soc.* 44, 1260-6(1922).—From X-ray data and space group reasoning it is shown that the crystals formed by adding ammonia to a soln. of Ni(NO<sub>3</sub>)<sub>2</sub> cannot have the compn. usually ascribed to them; careful chemical analysis proves them to be Ni(NO<sub>3</sub>)<sub>2</sub>·6NH<sub>3</sub>. These crystals have a structure similar to that of NiCl<sub>2</sub>·6NH<sub>3</sub> (cf. preceding abstract). The nitrate N atoms may, however, have the same sort of a displacement as have the sulfur atoms in pyrites. The length of the side of the unit cube is 10.96  $\text{\AA.}$

RALPH W. G. WYCKOFF

**The regularity of the molecular volumes of inorganic compounds.** FR. A. HENGLER. *Z. anorg. allgem. Chem.* 120, 77-84(1921); cf. *C. A.* 16, 1343.—W. Biltz has shown (*C. A.* 15, 198) that straight lines are formed when the mol. vols. of the halogen salts of the alkali metals are plotted as ordinates against numbers, as abscissas, which correspond to the anions (or cations). H finds this principal holds for the following groups of inorg. compds. Ag, Cu, and Tl chlorides, bromides, and iodides; K, Rb and Cs iodates, sulfates, and selenates, permanganates and perchlorates; Ca, Sr, Ba, and Pb chlorides bromides, iodides, carbonates, tungstates, sulfates, and sulfides; Ti, Zr and Ce oxides; Ag, Zn, Pb and Hg sulfides, selenides, and tellurides. From the linear equation  $y = ax + b$  of the graphs thus formed values for  $a$  and  $b$  are obtained from which



$y$  (mol. vol.) can be computed when  $x$  (the atomic or radical vol. of the anion or cation) is known. Similarly  $x$  may be computed when  $y$  is known. The values of  $a$  and  $b$  are characteristic for each group of salts having like crystalline form. The densities of *lithium, sodium and potassium fluorides* are 2.587, 2.726, and 2.669, resp. JACOB CORNOG

**The critical constants of mercury.** S. WEGNER. *Kgl. Danske Videnskab. Selskab. Math.-fys. Medd.* 3, No. 4, 12 pp. (1920).—The critical consts. of Hg have not been detd. directly on account of exptl. difficulties, the temp. involved being above the working limit of quartz app. However, by extrapolating the curves showing the densities of the liquid and satd.-vapor phases at different temps., the author deduces the following values: critical temp. =  $1450^{\circ}$ , critical pressure = 1086 atm., critical d. = 5.0. These values are confirmed by theoretical considerations. If curves be plotted giving the d. of liquid and vapor phases of mercury and hydrogen, the temp. and d. being written in terms of the critical temp. and d., it will be seen that the two curves practically coincide. Vapor-pressure curves plotted in a similar manner also coincide, from which the author concludes that *hydrogen* at this low temp. is monatomic. S. GULBRANDSEN

**Foundation of the Maxwell-Boltzmann distribution law.** A. WASSUTH. *Sitz. Akad. Wiss., Wien, Abt. IIa* 130, 159-66 (1921).—A mathematical paper. H. J. C.

**The kinetic theory of solids (metals) and the partition of thermal energy.** I. B. M. SGN. *Phil. Mag.* 43, 672-82 (1922).—Starting from known values of the sp. heat, compressibility, and the coeff. of linear expansion, S. has investigated the amplitude of mol. vibration and the intermol. forces. The partition of the gain of thermal energy is dealt with. For Cu, for example, (1)  $2.02 \times 10^{-16}$  erg is absorbed by each mol. to increase the energy of translational motion; (2)  $1.2 \times 10^{-16}$  erg is absorbed by the rotational motion, and presumably increases the energy of the electrons; (3)  $0.76 \times 10^{-16}$  erg is absorbed in doing work against the intermol. forces. II. *Ibid* 683-7.—The same method of treatment as used in part I is applied to systems of cubic and face-centered cube arrangement. The results are substantially the same. S. C. LIND

**The unsteady flow of gases through orifices.** A. FLÜGNER. *Vierteljahrs. Naturforsch. Ges. Zürich* 66, 71-86 (1922).—Equations and tables are given for the calcn. of the flow of a perfect gas through an orifice where the outer pressure is less than necessary for steady adiabatic flow. F. R. BICROWSKY

**Prehensility: a factor of gaseous adsorption.** H. BRIGGS. *Proc. Roy. Soc. Edinburgh* 42, 26-33 (1922).—The term prehensility is proposed to describe the function of adsorbents in producing high vacua where the conception of seizing hold of gas mols. is more pertinent than their retention. Prehensility is defined as the slope at the origin of an adsorption isotherm in which wts. of gas adsorbed per unit of adsorbent are plotted as ordinates and the corresponding pressure of the gas as abscissas. The max. prehensility was found with *plumstone charcoal*. Decreasing values were found for *birch charcoal, coconut charcoal, German charcoal* (impregnated with Zn and Fe), *colloidal SiO<sub>2</sub>* and *activated anthracite*. The theory of the high degree of vacuum obtainable by using a succession of charcoal bulbs is discussed. D. B. DILL

**A quantitative study of the adsorption in solution and at interfaces of sugars, dextrin, starch, gum arabic, and egg albumin, and the mechanism of their action as emulsifying agents.** GEO. L. CLARK AND WM. A. MANN. *J. Biol. Chem.* 52, 157-82 (1922).—Quant. measurements were made by the most accurate methods of surface tension, interfacial tension, and viscosity of solns. of these substances at all concns. both alone and in the presence of HCl, NaOH, NaI, Na<sub>2</sub>SO<sub>4</sub> or NaHCO<sub>3</sub>. A study was also made of actual emulsions made with each of the substances alone and in the presence of each of the electrolytes. Viscosity and ability to lower the interfacial tension are the two predominating factors in the emulsifying action of sugar with the former of primary importance. The chem. nature of the oil and also the chem. nature of the liquids being

emulsified influence the efficiency of sugar as an emulsifying agent. The inversion of sucrose is accompanied by a slight increase in surface tension but invert sugar is no more efficient than sucrose in holding up suspensoids or emulsoids. Dextrin is a better emulsifying agent than starch; viscosity and lowering of interfacial tension are again the predominating factors, with viscosity in this case, however, of secondary importance. Exptl. evidence was obtained that dextrin is of the same chem. nature as starch, being simply a more highly dispersed starch. Lowering of interfacial tension and viscosity produce favorable emulsifying conditions for solns. of gum arabic. The emulsifying action of egg albumin is related to film formation by adsorption at liquid interfaces and the best emulsions were obtained with it. "No one general rule can be made as to the effect which produces the best emulsions for any one substance, nor can any one generalization be made for the effect which produces best emulsions for all substances under all conditions. Those which seem to be of predominating importance are viscosity and film formation, the latter effect being of primary importance since it was with egg albumin, where a film formation is quite marked, that the best emulsions were obtained."

A. P. LOTHROP

The colloids arabic acid and arabic acid plus gelatin. F. W. TIEBACK. *Pharm. Weekblad* 59, 574-89(1922).—The ash content of arabic acid can be reduced to 0.1% by treatment with 0.05 N HCl, pptn. with EtOH, pressing out the ppt., repeating this operation several times, and finally dialyzing the aq. soln. 8 days in a parchment sack. The neutralization equiv. of the prepn. was 1210, corresponding to a mol. wt. of 2420. The cond. was greater than could be accounted for by the presence of slight impurity. At 18° a 1.2% soln. had a cond. of  $8.7 \times 10^{-4}$ . The temp. coeff. was 2.5, as is the case with most org. acids. A soln. of arabic acid and gelatin is flocculated by dil. HCl, further addition of which causes peptization. The flocculation occurs at a normality between  $10^{-4}$  and  $2 \times 10^{-3}$ .

A. W. DOX

The sol-gel equilibrium in protein systems. R. H. BOGUE. *J. Am. Chem. Soc.* 44, 1313-22(1922).—Expts. on the viscosity-plasticity relations in gelatin solns. showed (1) that, as measured by the MacMichael viscosimeter, gelatin in H<sub>2</sub>O follows the laws of viscous flow at elevated temps. and of plastic flow at lower temps. (above the solidification point); and (2) that the transition between the sol and the gel form does not take place at any given point of temp. but rather extends throughout a rather indefinite period of temp. At a given temp. (35°) the increase or decrease of viscosity with time depends upon the H-ion concn., the nature of the inorg. ions present and the amt. of hydrolyzed protein in the system. The temp. at which no change in viscosity with time is observable may not be taken as a critical temp. between the sol and gel forms but rather, given sufficient time under aseptic conditions, conditions may be reached at any temp. at which there will be no change in viscosity with further lapse of time. The expression "no change in viscosity with time" means only that the relative vol. of the particles of gelatin or gelatin aggregates in the system tends neither to increase nor decrease under the conditions attained. A lowering of the temp. will cause an increase in this relative vol. and hence an increase in viscosity, but this increase having been attained (after the lapse of time), the viscosity will then again become const. A rise in temp. will produce the opposite effect. The equation, therefore, is  $\eta_{sp}/c = K/f(T)$ , indicating that the viscosity of pure gelatin at any given H-ion concn. is inversely proportional to some function of the temp. and that, at equil., there will be some viscosity (at any given H-ion concn.) which will correspond with every point of temp. There is no sharp transition point between the sol and gel forms in protein systems, but the transition is continuous and reversible over a somewhat indefinite period. C. A. R.

The structure of elastic gels. R. H. BOGUE. *J. Am. Chem. Soc.* 44, 1342-56 (1922).—The several theories of gel structure are discussed; many contemporary

investigations support the catenary or fibrillar structure hypothesis proposed by B. in 1920. The premises of this theory are that the sol consists of slightly hydrated or swollen mols. united into short chains. When the temp. falls, the threads increase in length and no. and their power of  $H_2O$  absorption increases, resulting in an increase in viscosity. A solid jelly results when the relative vol. occupied by the swollen mol. threads has become so great that freedom of motion is lost, and the adjacent heavily swollen aggregates cohere. The rigidity is dependent upon the relative amt. of free solvent in the interstices of the aggregates and on the amt. of solvent that has been taken up by the gelatin in a hydrated or imbibed condition. The resiliency or elasticity is dependent upon the length and no. of catenary threads. Soln. is the reverse of gelation. Swelling is detd. by osmotic forces and the Donnan equil. The influence of electrolytes, of varying H-ion concn. and of the valence of the combining ion upon several of the characteristic properties of gelatin gives additional evidence in support of B.'s theory, as do also Smith's data on the mutarotation of gelatin. Loeb's occlusion theory is not out of harmony with B.'s theory but rather explains the distribution of absorbed water and its variation with the H-ion concn. mathematically in terms of the Donnan equil.

C. A. R.

**The electrical precipitation of colloids.** C. H. HALL, JR. *J. Am. Chem. Soc.* **44**, 1246-9(1922).—Investigations were made of the effect of high potentials upon colloidal suspensions in non-conducting liquids. No pptn. was detected in the range  $10^4 - 2 \times 10^5$  v., either a. c. or d. c. The failure of pptn. of sols was investigated mathematically and it was shown that the rate of pptn. would be  $1/20000$  of that for smoke for the same energy applied to the particle.

HARRY B. WHISER

**Clays as dispersed systems.** SVEN ODEN. *Trans. Faraday Soc.* **17**, 327-48(1922).—No given chemical component is necessary, in order to classify a soil as a clay. A soil layer is a clay, a silt or a sand soil according to whether the greatest part falls within the limits for clay, loam, or sand. These limits are detd. by size of particles. Clays are disperse formations of mineral fragments in which particles of smaller dimensions than  $2 \mu$  predominate. Oden detd. the distribution of sizes of particles by collecting the particles settling through a tall cylinder of water on to a plate suspended near the bottom of the cylinder by a fine gold wire. The upper end of the gold wire was attached to the left pan of a balance fitted with an elec. appliance which automatically added successive equal wts. to the right pan when the accumulated sediment equalled the wts. already added. A second device recorded the time at which each wt. was added. The formula for calcg. the effective radius  $r$  of the particles is,  $r = \sqrt[3]{(3/4\pi)(v\phi/\pi n)}$  in which  $v$  is the vol. in  $cm.^3$ ,  $\phi$  the number of g. of suspension per  $cm.^4$ ,  $s$  the sp. gr. (always taken as 2.7) and  $n$ , the number of particles in volume  $v$ . The method for applying this equation to a soil suspension is shown. By using suspending media having different densities and viscosities practicable rates of deposition of sediments from the finest particles up to those  $50 \mu$  in radius are possible.

F. E. BROWN

**The solubility of small particles and the stability of colloids.** L. F. KNAPP. *Trans. Faraday Soc.* **17**, 457-65(1922).—In the presence of an excess of the substance of which the disperse phase is composed, colloidal particles are uniform in size. This is due to the fact that the soly. of particles of this size is the same as the soly. of the large undispersed body. This soly. is due to the combined effect of surface tension and the elec. charge on the surface of the particle. An equation is derived for the value of  $r$  the "critical" radius of such suspended particles.  $r = \sqrt[3]{(q^2 d/8\pi K\sigma)}$  in which  $q$  is the elec. charge on a particle,  $d$  the distance between the double elec. layers (Helmholtz),  $K$  the dielec. const. of the dispersion medium and  $\sigma$ , the interfacial tension between the suspended particle and the dispersion medium. AgBr pptd. in gelatin forms in various small-sized particles. But after 40 min. heating the grains are uniform and larger than the

largest particles first formed. To explain this increase in size one must assume either that the charging of the particle is a gradual process of adsorbing ions, or that the complete pptn. of the AgBr is delayed by the gelatin. In this case there is no plane surface so the final size must be the size of minimum soly. The article is largely mathematical.

F. E. BROWN

**Measurement of the viscosity and surface tension of an emulsion colloid.** HEDWIG WALTER. *Sitzb. Akad. Wiss., Wien, Abt. IIa* 129, 709–20 (1920).—Investigations were carried out on the degree of dispersion, viscosity and surface tension of colloidal solns. of gum arabic of varying concns. In all colloids the particles of the disperse phase were amicros. The viscosity was found to depend on the concn. and temp. of the colloid in accord with the formula of Einstein (*Ann. Physik* 19, 289) indicating that the disperse phase was liquid. The functional relationship between the coeff. of friction and concn. or temp. was expressed approx. by empirical formulas. The surface tension of the colloids and the temp. coeff. of surface tension were measured by Jaeger's method (*Sitzb. Akad. Wiss., Wien* 105, 425 (1896)) and the consts. of a formula proposed by Jaeger were detd. The capillarity-concn. curves revealed the dependence of surface tension on the degree of dispersion of the colloidal particles. HARRY B. WEISER

**The solubility of crystallized strontium hydroxide.** D. SIDERSKY. *Bull. assoc. chim. suc. dist.* 39, 167–77 (1921).—The hydroxide was prepd. by calcination of strontianite, treatment with hot water, filtration and crystn. It was purified by 3 further crystns. Two procedures were followed: (1) The base, in excess, was placed in water and the temp. raised to the desired point. (2) An excess was placed in water above the desired point and then cooled. The SrO content was detd. by titration with N HCl, phenolphthalein being used. Detns. were made at 25 temps. from 0° to 101.2°. A curve is given and a table calcd. for the soly. at each degree for both SrO and  $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  in 100 g. and in 1 l. of soln. Solys. were then detd. at 3°, 15°, 24°, and 40° in solns. contg. 20, 50, 100, 150, 200 and 250 g. purified sucrose, resp. A curve shows that at each temp. the soly. of SrO increases with the sucrose in arithmetical ratio. A table is compiled showing the soly. of SrO at each of the 4 temps., for all percentages of sucrose from 1 to 25. If  $P$  equals % sucrose per g. of soln. and  $S$  % SrO, then at 15°,  $S = 0.56 + 0.091 P$  and at 24°,  $S = 0.77 + 0.133 P$ . I. D. GARARD

**Influence of electrolytes on the solubility of non-electrolytes.** A. McKNOWN. *J. Am. Chem. Soc.* 44, 1203–9 (1922).—The heats of soln. of ether in various solns. of NaCl have been calcd. from Thorne's soly. data at 15° and 25° (*C. A.* 15, 1842) by means of a relation between soly., heat of soln., and temp. of the form of the van't Hoff isochore. Statistical treatment of the phenomena of soln. and pptn. leads to an expression for soly.,  $s = Ae^{Q/RT}$ , which is in agreement with the isochore relation above. The salting-out effect on ether of NaCl depends on the specific influence of the cation and anion, the relative influences being  $-21.7$  to  $+671$  with the anion predominating. JAMES M. BELL

**Measurement of solubility by floating equilibrium.** The solubility of lead acetate. M. L. DUNDON AND W. E. HENDERSON. *J. Am. Chem. Soc.* 44, 1196–1203 (1922).—The method consists in adding a known wt. of solvent to a satd. soln. of unknown compn. until the soln. attains the same d. as a float calibrated at a definite arbitrary temp. This method is capable of giving rapid and accurate results. The soly. of  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$  is given for 5° intervals from 0 to 50°. It seems probable that a slight variation in results at the higher temps. is due to the partial formation of basic salts. J. M. B.

**The coalescence of solids.** A. A. POLLITT. *Chem. Age* (London) 6, 545–7 (1922).—Vapor pressure in liquid drops varies with the curvature, increasing as the latter increases. From this consideration it follows that a small drop will distill over and condense on a larger drop in its immediate vicinity. This phenomenon has been noted

for liquids and for iodine crystals. Very finely powdered material has a higher vapor pressure, a greater soly., and a lower m. p. than the same material in bulk or in coarse crystals. When a plate is broken cleanly, without chipping, the two pieces will fit together perfectly and should cohere were it not for a thin film of air which serves to prevent contact at all of the points. It is possible to polish copper to such an extent that a cube of it will support eleven others which are merely placed in contact with it. Freshly split mica can be made to coalesce by pressure of the fingers. "Sintering" defines those cases of coalescence which occur without fusion or at least with only very slight fusion; "fritting" indicates that the product is distinctly vitreous, and that the coalescence has been accompanied by marked fusion. The manuf. of bricks and pottery involves the first process, while the production of the glaze upon them is an example of the latter. Other cases of coalescence in solids are the use of oil and tar as bonding materials in road-making, the welding of metals at temps. far below their melting points, and the agglomeration of ppts. on standing. The effect of liquid added to finely divided solid particles is illustrated by the familiar example of moist sand and the expts. of Reynolds. Liquid drops and solid grains will coalesce provided they are brought into actual intimate contact. Conversely, to prevent coalescence a film must be formed on the surface of the drops, as in the case of oil emulsions in soapy water. J. T. R. A.

The molecular separation in crystals and Bravais' rule. M. VOLMER. *Physik. Z.* 22, 646-7(1921).—A dynamic picture of a qual. nature is suggested to account for Bravais' rule, according to which the rate of growth normal to a crystal face is a minimum for those planes which are densest in atoms. Various factors which will influence the rate of growth on different faces are also mentioned. RALPH W. G. WYCKOFF

Tensions and pressures in surfaces and "cleavage planes" of a fluid: swelling. H. HULSHOF. *Ann. Physik.* 67, 278-300(1922).—A mathematical paper seeking to explain the phenomenon of swelling. This is viewed as a capillary phenomenon; the point of departure is the assumption that the sum of the exerted pressure and the molecular attraction at any point in a fluid has the same value in all directions, and, just as the entropy, can be detd. from a knowledge of only the temp. and density at the point.

A. E. STEARN

Capillarity. I. Some general considerations and a discussion of methods for the measurement of interfacial tension. A. FERGUSON. *Trans. Faraday Soc.* 17, 370-83 (1922).—No data are given. Twenty methods for measuring surface tension are mentioned. Of these methods, capillary rise, pendant drop, or bubble, and sessile drop are mathematically analyzed. The surface tension of solids may be detd. either by change of soly. with size of particle, or change of vapor pressure with change of size of the particles considered. II. A modification of the capillary-tube method for the measurement of surface tension. A. FERGUSON AND P. E. DOWSON. *Ibid.* 384-91.—The modification described consists in measuring the total pressure " $p_a$ " above a meniscus in a capillary tube immersed in the liquid whose surface tension is to be detd.  $p_a = P + g\rho h + (2T/R)$ .  $P$  is the atm. pressure;  $\rho$ , the density;  $h$ , the depression of the meniscus below the surface of the liquid;  $T$ , the surface tension; and  $R$ , the radius of curvature at the vertex of the meniscus. The surface tension of benzene was found to be 29.58 dyne-cm.<sup>-1</sup> at 15°. Benzene is not considered a good standard liquid, for it showed a surface tension of 29.6 dyne-cm.<sup>-1</sup> after careful purifying and additional crystn., and the same samples after a few days showed a surface tension of 29.9 dyne-cm.<sup>-1</sup>.

F. H. BROWN

Surface tension of soap solutions for different concentrations. A. L. NARAYAN AND G. SUBRAHMANYAM. *Phil. Mag.* 43, 663-71(1922).—Two exptl. methods are employed to measure the surface tension: (1) the usual capillary method; (2) a sensitive manometric method of measuring directly the pressure prevailing within the soap

bubble by means of an inclined manometer with xylene as fluid. The results of both methods are in agreement from about 0.5 to 0.03 of satn., and show that over the entire range of concns. in which bubbles can be blown the surface tension is const., having a value of approx. 23 dynes per cm. At still lower concns. only the capillary method is applicable. For a Castile soap soln. the surface tension begins to rise at 0.2 g. per 100 cc. of soln. and continues to rise rapidly at the lower concns., approaching the value for water asymptotically. The agreement of the two methods shows that the angle of contact is 0, as has been proved experimentally by other investigators. S. C. LIND

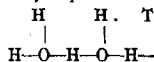
**Thermodynamical theory of surface tension.** S. SANO. *Phil. Mag.* 43, 649-58 (1922).—Mathematical development of a thermodynamic theory of surface tension in the transition layer between two fluids, based on a number of assumptions, some of which are entirely arbitrary. S. C. L.

**Negative viscosity.** A. I. RABINOVICH. *J. Am. Chem. Soc.* 44, 954-65 (1922).—An attempt is made to explain the phenomenon wrongly named "negative viscosity." It cannot be a result of the low viscosity of the solute, for the viscosities of the fused salts are invariably high. Hydration increases the viscosity instead of lowering it. The formation of complex ions or mols. would have the same effect. The influence of the elec. field produced by ionization cannot possibly diminish the viscosity. The depolymerization of the solute may indeed lower the viscosity of the soln., but this effect cannot be very important, considering the high viscosity of the solute. R. therefore concludes that the depolymerization of the solvent is alone adequate to explain negative viscosity. Cryoscopic measurements show that in fact the molar wt. of water in AcOH falls as the amt. of AcOH is increased. Colorimetric evidence of the depolymerization of the solvent is also given. As causes of the depolymerization he suggests the effect of the vol., the hydration, and the high dielec. const. of the solute. Cf. *Fluidity and Plasticity*, pp. 178-188 (Bingham). E. C. BINGHAM

**Diffusion of solutions.** T. H. LITTLEWOOD. *Proc. Phys. Soc. (London)* 34, 71-6 (1922).—An optical method is described for finding the concn. at various depths in a diffusing soln. The soln. is contained in a closed vessel whose top and one side are of glass. On the glass side is a vertical scale. This vessel is immersed in another filled with water and contg. a mirror which can be rotated and whose position is read on a graduated scale. On a horizontal sliding stand is a telescope which carries a horizontal wire illuminated by Na light. The mirror is adjusted so that the image of the wire, after twice passing through the liquid, is seen on the cross wires of the telescope. The corresponding division of the vertical scale is also observed. From these measurements the concn. can be detd. at different depths. Sufficient data for calcg. the coeff. of diffusion can be obtained in less than a day. C. C. VAN VOORHIS

**Constitution and function of electrolytes.** W. MADELUNG. *Ann.* 427, 35-109 (1922).—This is a theoretical discussion of the constitutional causes which det. the formation and stability of electrically charged at. aggregates (ions) in crystals and in soln. Hantzsch's theory of  $\psi$ -isomerism is discussed and extended. The CN compds. described by Hantzsch are  $\psi$ -acids in their non-ionizable forms and true acids in the forms corresponding with their salts. Corresponding with  $\psi$ -acids and  $\psi$ -bases a class of  $\psi$ -salts can be recognized as falling within the same view of  $\psi$ -isomerism.  $AlCl_3$  and  $SnCl_4$  are not ionized as such and are therefore  $\psi$ -salts. In general the uni- and some bivalent metals tend to form salts, while most of the ter- and quadrivalent metals form  $\psi$ -salts. The Na compd. of  $AcCH_2COMe$  is an electrolyte and non-volatile, like NaCl, while the Al deriv. is a nonelectrolyte and is volatile, like  $AlCl_3$ ; both the Na compds. are salts and both the Al compds. are  $\psi$ -salts. In order to form ions, the ter- and quadrivalent metals have to combine with other ions or mols. to form centrally orientated complexes, such as  $[Fe(OH)_4]^{--}$ ,  $[SnCl_4]^{--}$ , etc. Ionization is, therefore, largely a

matter of the formation of these complexes. In acids, it is assisted by the accumulation of a no. of electro-negative peripheral groups around the nuclear atoms, as above. In bases, the accumulation of H atoms as such, as  $\text{NH}_2$ - or HO-groups, or as  $\text{H}_2\text{O}$  or  $\text{NH}_3$  mols., has a similar effect. Even C may become the central atom of an ion if sufficiently loaded with electrically powerful groups; the ion of guanidine is represented by the formulá  $[\text{C}(\text{NH}_2)_3]^+$ , which expresses its strongly basic character much better than the customary formula based on the integral valencies of org. chem. Tert.-butyl iodide,  $(\text{CH}_3)_3\text{CI}$ , is better termed trimethylcarbonium iodide, as it is ionized in soln. in liquid  $\text{SO}_2$ , a remarkable instance of the tendency of a large accumulation of H atoms to promote ion formation; the ions  $[\text{C}(\text{CH}_3)_3]^+$ ,  $[\text{C}(\text{NH}_2)_3]^+$ , and  $[\text{CO}_3]^+$  are strictly analogous. Apparently simple ions,  $\text{H}^+$ ,  $\text{OH}^-$ ,  $\text{NO}_3^-$ , are subject to the same laws regarding the tendency to centric orientation and the influence of the peripheral groups. H and HO ions are invariably combined with at least 1 mol.  $\text{H}_2\text{O}$  and often with more. By assuming a further degree of hydration, chains may be produced which are strongly reminiscent of the structure of the cryst. compd:



of peripheral groups is often felt, not only in the circumjacent atoms but also in more remote parts of the mol. This phenomenon is termed *induction*; it is illustrated by many examples.

C. J. WEST

**Decomposition of nitrous acid.** A. KLEMENC AND F. POLLAK. *Z. physik. Chem.* 101, 150-71(1922).—The velocity of decompn. of  $\text{HNO}_2$ , measured by the decrease in the  $\text{KMnO}_4$  titer, depends on the rate at which the NO escapes from the soln. The latter detcs. the velocity of the process. The velocity of decompn. depends, therefore, on the NO-pressure above the soln. On the assumption that a considerable NO-pressure is due to the undissociated acid, it follows that the velocity of decompn. is proportional to the undissociated  $\text{HNO}_2$ . This assumption has been confirmed exptly. On the basis of the "invasion" and "evasion" coeffs. of  $\text{CO}_2$ , as measured by Bohr, it is shown that in  $\text{H}_2\text{O}$  the concn. of free NO is approx. equal to the undissociated  $\text{HNO}_2$ . If NO is led through an aq. soln. of  $\text{HNO}_2$  the velocity of decompn. is increased. The velocity of the direct decompn. of  $\text{HNO}_2$  cannot be detd. by the exptl. method used; it is probably immeasurably fast. In solns. of mineral acids the velocity const. increases with the acid concn.

H. JERMAIN CREIGHTON

**Chemical equilibrium.** ROBERT KREMANN. *Fortschritte Chem.* 17, 1-22, 65-80 (1921).—Progress in 1919 and 1920.

C. C. DAVIS

**Chemical reaction rates.** ROBERT KREMANN. *Fortschritte Chem.* 17, 23-32, 81-3(1921).—Progress in 1918 and 1920.

C. C. DAVIS

**Studies on the reaction kinetics of the influence of ammonia on aromatic aldehydes.** FRIEDRICH DOBLER. *Z. physik. Chem.* 101, 1-33(1922).—Ammonia can be titrated against HCl in the presence of hydramides, with hematoxylin as an indicator. This method has been employed to measure the velocity of the reaction between  $\text{NH}_3$  and aromatic aldehydes in alc. soln. The following aldehydes were employed: benzaldehyde, *p*-tolualdehyde, *m*-xylaldehyde, anisaldehyde and cinnamaldehyde, as well as *p*-chloro-, *o*-, *p*- and *m*-nitrobenzaldehyde. For the most part the reactions were studied at  $20^\circ$ . For a certain time the formation of hydrobenzamide at  $20^\circ$  is a bimol. process. In the majority of instances the formation of the corresponding hydramides from the above-mentioned aldehydes follows the 2nd reaction order. The reaction with benzaldehyde and with *p*-tolualdehyde was studied at  $10$ ,  $20$ ,  $30$  and  $40^\circ$ . The velocity of both reactions is about doubled for each  $10^\circ$  rise in temp. In the formation of the hydramide the following equil. is established: aldehyde +  $\text{NH}_3 \rightleftharpoons \text{H}_2\text{O}$  + hydramide. With increase in temp. the position of equil. is displaced towards the right. The accel-

erating and retarding influence of  $C_6H_5CO_2H$ ,  $(NH_4)_2SO_4$  and  $NaOH$  has been studied. It has been concluded that these influences depend on the change brought about in the dissociation of the  $NH_4OH$ . Decrease in the  $OH$ -ion concn. increases the velocity of the reaction, and *vice versa*. Double linkings, as well as  $Cl$  as a  $p$ -substituent in the nucleus of the aldehyde, increase the velocity of the reaction 6- and 3-fold, respectively. The introduction of the  $Me$  group in the nucleus increases the velocity, while a 2nd similar substitution in the  $o$ -position brings about a decrease. The  $CH_3O$  in  $C_6H_4(CH_3O)CHO$  decreases the velocity to about 0.5 that with benzaldehyde. The  $NO_2$  group in the  $m$ -position increases the velocity appreciably, while the same substituent in the  $o$ - and  $p$ -position acts in the opposite manner.

H. J. C.

**Formation and hydrolysis of lactones.** II. ANTON KAILAN. *Z. physik. Chem.* 101, 62-93(1922); cf. *C. A.* 14, 1777.—The velocity of the autocatalytic formation of lactones in aq. soln. is nearly proportional to the  $H$ -ion concn. Henry's results with  $Ag$  salts of hydroxy acids, which deviate from this rule, must be due to impurities in his solns. The same relation holds for the formation of lactones from  $CH_3ClCO_2H$ . With  $HCl$  as catalyst, the velocity is proportional to the total concn. of the acid up to a concn. of 0.2  $N$ . If an independent catalytic action of the undissociated  $HCl$  mols. is assumed, this must be of the same magnitude as that of the  $H$  ions ( $k_{HCl} = k_{H^+}$ ). On the other hand with higher acid concns., the velocity increases more rapidly than the  $H$ -ion concn., but more slowly than the total acid concn., showing that under these conditions the action of the  $HCl$  mols. must be less than that of the  $H$  ions, a result that is difficult to explain. This difficulty is removed if it is assumed that only the  $H$  ions have an independent catalytic action, and that the deviation from proportionality between the velocity of reaction and the  $H$ -ion concn. is due to a change in the activity of the  $H$  ions through the addn. of  $HCl$ . The increase in the velocity of the reaction brought about by the addn. of  $KCl$  to the  $HCl$  is attributed to a repression in the dissociation of the latter. No relation has been found between the velocity of the reaction and the activity coeff. In alc. of 99% by vol. lactonization of  $\gamma$ -hydroxyvaleric acid proceeds much faster both in the presence of  $HCl$  and in the absence of a catalyst than in  $H_2O$ . The latter exerts a marked retarding action as in esterification. The velocity decreases rapidly as the  $H_2O$  content of the alc. is increased. In the case of autocatalytic lactone formation in 99% alc., the velocity of reaction can be only partially attributed to the  $H$  ions present.

H. JERMAIN CREIGHTON

**Reaction mechanism of permanganate reduction and its physicochemical foundation.** I. The reaction permanganate-formic acid in weakly acid solution. J. HOLM-LUTA. *Z. physik. Chem.* 101, 34-53(1922).—The velocity of the reaction has been measured at 15, 22 and 25°. The order of the reaction has been detd. by van't Hoff's method and the mean value 2.14 obtained. From the results of the expts. it is concluded that the reduction of  $HCO_2H$  by  $MnO_4^-$  in weakly acid soln. takes place in accordance with the following scheme: (1)  $2(MnO_4^- + HCO_2^- = MnO_4^{--} + H^+ + CO_2)$ , measurably slow; (2)  $2MnO_4^{--} + 8H^+ + 5HCO_2^- = MnO_4^- + Mn(HCO_2)_6^{--} + 4H_2O$ , instantaneous; (3)  $Mn(HCO_2)_6^{--} = Mn^{+++} + 5HCO_2^-$ , equil.; (4)  $2Mn^{+++} + HCO_2^- = 2Mn^{++} + H^+ + CO_2$ , faster than 1; (5)  $2(2Mn^{+++} + 4H_2O = Mn^{++} + Mn(OH)_4 + 4H^+)$ , immeasurably fast; (6)  $MnO_4^- + 4Mn^{++} + 8H^+ = 5Mn^{+++} + 4H_2O$ , immeasurably fast; (7)  $2(Mn(OH)_4 + 4H^+ = Mn^{+++} + 4H_2O)$ , equil.; (8)  $2(Mn^{+++} + HCO_2^- = Mn^{++} + H^+ + CO_2)$ , very slow. The summation of these reactions gives the empirical reaction,  $2MnO_4^- + 11H^+ + 5HCO_2^- = 2Mn^{++} + 5CO_2 + 8H_2O$ .

H. JERMAIN CREIGHTON

**The significance of the second dissociation constant of uric acid for the equilibrium of monourate solutions.** A. KANITZ. *Z. physiol. Chem.* 116, 169-86(1921).—From the data of Kohler and the equation  $[Monourate]^2/[Diurate] \times [Uric\ Acid] = k_1/k_2$



where  $k_1$  and  $k_2$  are the first and second dissociation consts. of uric acid the hitherto unknown value of  $k_2$  has been calcd. to be  $2.6 \times 10^{-9}$ . In a monourate soln. about 3.35% is present as free uric acid, 3.35% as diurate and 93.3% as monourate. Such a soln. is practically neutral. In a diurate soln. about 1.57% is hydrolyzed; the OH<sup>-</sup> ion concn. is about  $1.57 \times 10^{-4}$ .

R. L. STUELLS

The cathodic reduction of elementary nitrogen. FR. FICHTER AND R. SUTER. *Helvetica Chim. Acta* 5, 246-55(1922).—The assimilation of elementary N by certain bacteria may possibly be of the nature of a reduction of the N to NH<sub>3</sub>. To test this viewpoint, F. and S. have studied, at ordinary temp., the cathodic reduction of N<sub>2</sub> dissolved under a pressure of 100 or 200 atm., in 1% H<sub>2</sub>SO<sub>4</sub>. With a Hg cathode, and 100 atm. N pressure, no certain reduction of N to NH<sub>3</sub> was observed. With a freshly and thickly platinized Pt cathode of large surface, having 0.6305 g. Pt-black, 0.33 mg. NH<sub>3</sub> was produced in 156 amp. min. at 200 atm. N pressure. The duration of this run was 8 hr., the mean current 0.325 amp., and the cathode current d. 0.0072 amp./cm.<sup>2</sup>. Attempts to increase the yield by using larger current d. gave smaller rather than larger yields. Increasing the duration of the expt. ceased to give larger yields after a certain length of time as the Pt-black loses its catalytic activity because of the coarsening of its grains. Increasing the N pressure would seem to be the only way of obtaining a greater yield of NH<sub>3</sub>, but this was not feasible with the particular bomb used. An attempt to oxidize N<sub>2</sub> dissolved under 100 atm. in an alk. electrolyte, on a platinized Pt anode, gave a negative result. A mixt. of N<sub>2</sub> and H<sub>2</sub> dissolved under pressure in 1% H<sub>2</sub>SO<sub>4</sub> did not combine catalytically on platinized Pt when no current was passing.

R. H. LOMBARD

Reducing and oxidizing action by alternating currents. A study of reaction kinetics in heterogeneous systems. O. COLLENBERG AND S. BODFORSS. *Z. physik. Chem.* 101, 117-49(1922).—The dissoln. of metals in solns. of ferric alum proceeds in accordance with the theory of Nernst, the velocity being that of a unimol. reaction. With the exception of Zn, the velocity consts. for the metals used (Cu, Cd, Sn and Fe) are almost equal, notwithstanding the very different electrochem. differences of the metals. The product of the viscosity of the soln. and the velocity const. is const., except with Zn. In a.c. electrolysis of solns. of ferric alum with electrodes of the above metals, the influence of the frequency is small within the limits studied (98-533). The a. c. does not change the course of the reaction between the metal and the alum soln.; it only effects a small increase in the yield.

H. JERMAIN CREIGHTON

Catalysts and chemical equilibrium. J. CLARENS. *Bull. soc. chim.* 31, 299-307 (1922).—A study of the reactions involved in Deacon's process was carried out to show that a catalyst may alter the equil. of the reaction. The reactions are (1)  $4\text{HCl} + \text{O}_2 = 2\text{H}_2\text{O} + 2\text{Cl}_2$  and (2)  $2\text{H}_2\text{O} + 2\text{Cl}_2 = 4\text{HCl} + \text{O}_2$ . If the CuCl<sub>2</sub> catalyst does not alter the equil. it must have the same influence on the velocities of (1) and (2). The reactions were carried out in a glass tube in a combustion furnace. The catalyst was supported by glass wool. The Cl<sub>2</sub>-water vapor mixts. were made by bubbling Cl<sub>2</sub> through H<sub>2</sub>O, the H<sub>2</sub>O-HCl mixts. by bubbling O<sub>2</sub> through fuming HCl soln. The exit gases were collected in suitable absorbing solns. and analyzed for HCl and Cl<sub>2</sub>. In the case of Cl<sub>2</sub> and H<sub>2</sub>O, reaction takes place to a certain extent in the absence of catalyst, the CuCl<sub>2</sub> is an active catalyst when fresh, but rapidly decreases in activity until it becomes inert. With O<sub>2</sub> and HCl there is no reaction in the absence of catalyst, the CuCl<sub>2</sub> is a very active catalyst and does not lose its activity with use. It is concluded that the CuCl<sub>2</sub> has a different effect on the reaction velocities of (1) and (2) and that there is no reason to believe that a catalyst has an equal influence on the velocities of 2 inverse reactions.

F. L. BROWN

The catalytic activity of copper. III. W. G. PALMER. *Proc. Roy. Soc. (London)*

101A, 175-86(1922); cf. C. A. 15, 3923.—The catalytic dehydrogenation of EtOH was studied by means of a *mixed catalyst* consisting of CuO and one of the following: Fe<sub>2</sub>O<sub>3</sub>, ZnO, MnO, MgO. The catalyst was prep'd. by dropping a soln. of CuSO<sub>4</sub> and the sulfate of the second oxide from a buret into boiling 10% Na<sub>2</sub>CO<sub>3</sub> soln., washing the ppt. until the Na flame test was no longer observed, and drying. The oxides were applied to the gas mantle support previously employed by moistening the mantle with oleic acid, applying the mixed oxide, and igniting to redness in the Bunsen flame in such manner that the CuO was reduced to Cu within the flame and oxidized to CuO again on removing. Each mantle was given 3 such treatments. Two of these catalysts prep'd. from the same mixt. of oxides gave results reproducible within 3%. Immediately before an expt. the catalysts were reduced in CO at 205°. The temp. was then raised to 260° and the alc. vapor passed in. The activity of the catalyst was const. for 75 to 80 min., then decreased. MgO and MnO were found to act as *promoters* when present in amts. greater than 2.5 and 0.4 at. %, resp. The other oxides gave less catalytic activity than pure CuO. MgO is a much more powerful promoter than MnO. The results are discussed from the standpoint of a combination of the *adsorption and the radiation theories of catalysis*. The requirements of a promoter are considered to be (1) transparency to the radiation from the main catalyst, (2) higher adsorbing power than the main catalyst.

F. I. BROWNE

The mechanism of the hydrogen-oxygen reaction catalyzed by platinum: and the application of titanium sulfate in its control. K. A. HOFMANN. *Ber.* 55B, 1265-74 (1922); cf. C. A. 16, 1897.—With Pt as contact material sat'd. with H<sub>2</sub> and surrounded with acid contg. dissolved O<sub>2</sub>, measurable quantities of peroxide are formed only when the activation of the H<sub>2</sub> is poor. The activation depends on previous satn. of the Pt with O<sub>2</sub>. Probably the reaction between H<sub>2</sub> and O<sub>2</sub> is represented by both equations (1) O<sub>2</sub> + 2H = H<sub>2</sub>O<sub>2</sub>, and (2) H<sub>2</sub>O<sub>2</sub> + 2H = 2H<sub>2</sub>O. Under favorable conditions the speed of (2) is very rapid. For prep'n. work where reductions with activated H<sub>2</sub> are employed, it is recommended to use an acid soln. of titanic sulfate to follow the activity of the system by the amt. of peroxide formation.

A. F. STRAEN

Purification of gases from methane. G. R. FONDA AND H. N. VAN AERENEM. *J. Ind. Eng. Chem.* 14, 539-40(1922).—The equil. const. for CH<sub>4</sub> at low partial pressures in an inert gas passed over a powd. Ni catalyst was found to be the same as at atm. pressure. Under the same conditions of temp. and flow an equal vol. of CuO gives less than 1/3 the decompn. caused by Ni.

G. R. FONDA

Change of properties of substances on drying. H. B. BAKER. *J. Chem. Soc.* 121, 568-74(1922).—After careful and extended drying by the agency of P<sub>2</sub>O<sub>5</sub>, the b. ps. of Br, Hg, C<sub>6</sub>H<sub>6</sub>, C<sub>6</sub>H<sub>14</sub>, CS<sub>2</sub>, CCl<sub>4</sub>, Et<sub>2</sub>O, MeOH, EtOH, and C<sub>2</sub>H<sub>5</sub>OH show a considerable rise. In most cases the time of drying was from 8 to 9 years, and the rise in b. p. ranged from 14° to 62°, with an av. of 42°. The hypothesis that this change in phys. property is caused by increased mol. complexity receives support from preliminary detns. of the surface tensions of dried liquids. The m. ps. of S and I show rises of 5.5° and 2.0°, resp., after 9 years drying. No change in d. could be observed in the cases of seven liquids dried for one year in contact with P<sub>2</sub>O<sub>5</sub>.

J. T. R. ANDREWS

Sodium, potassium and their lustrous alloy in nitrogen. G. BORNEMANN. *Z. angew. Chem.* 35, 227(1922).—A method, probably originating with Bunsen in the Heidelberg lab., for obtaining lustrous alkali metals or their alloys. A clean, dry glass tube, about 15-20 mm. wide is sealed at one end, and about 20 cm. above this point it is drawn out to a diam. of 3-4 mm. A clean metal sieve (1-mm. mesh) is placed at the constriction so as to press against the sides of the tube. Freshly cut Na or K (or a mixt. of these metals) is placed on the sieve, and the tube then sealed about 20 cm. above the constriction. The metal forms oxide, and the latter absorbs CO<sub>2</sub>, leaving

finally only N in the tube. After some hrs. melt the metal carefully, holding the tube horizontally so as to prevent the metal from running through the sieve. Allow to cool and stand for some time. If the metal surface remains bright remelt carefully, holding the tube in an upright position, and heating at first from the wire sieve down to the constriction, and later up to the metal. Upon melting the metal flows through the sieve, but carbonates, hydroxides, etc., do not. Finally seal off the tube at the constriction. Alloys contg. 25-90% of K may be prepd. which remain liquid at room temps., and are ordinarily oxidized with ease. W. C. EBAUGH.

The absolute affinity of benzoic acid and of the three toluic acids for the same base. H. N. K. RÖRDAM. *Kgl. Danske Videnskab. Selskab. Math.-fys. Medd.* 3, No. 7, 32 pp. (1920).—Great exptl. difficulties are involved in detg. the abs. affinity in reactions between org. compds. Very few data along this line are available, although such data would throw considerable light on the energy of formation of org. compds. and on the structure of org. radicals. Our ideas in this field are now mainly based on speed of reaction, which is often influenced by catalytic action. R. detd. the abs. affinities between  $\text{Ag}_2\text{O}$  and benzoic, *o*-, *m*- and *p*-toluic acids, thus revealing the changes in free energy in the benzene radical by the introduction of the Me group in the *o*-, *m*- and *p*-positions. This was accomplished by the detn. of e.m.f. in the following system:

$\text{Ag} \left| \begin{array}{c} \text{AgX(solid)} \\ \text{HX(solid)} \end{array} \right| \text{acid soln.} \left| \text{H}_2 \right| \text{alk. soln. } \text{Ag}_2\text{O} \left| \text{Ag} \right.$  where HX is the org. acid and AgX its salt. Actually this detn. was carried out in 2 stages, namely: (a)  $\text{Ag} \left| \text{Ag}_2\text{O, alk.} \right.$

$\text{soln.} \left| \text{H}_2 \right.$  and (b)  $\text{Ag} \left| \begin{array}{c} \text{AgX(solid)} \\ \text{HX(solid)} \end{array} \right| \text{acid soln.} \left| \text{H}_2 \right.$  E.m.f. of element (a) at  $25^\circ = 1.143 \text{ v.}$ , while the results with the various elements in group (b) were: benzoic acid 0.911 v., *o*-toluic 0.933 v., *m*-toluic 0.914 v., and *p*-toluic 0.913 v. By subtracting in turn the voltage of (b) elements from that of (a) the e.m.f. of  $\text{Ag}_2\text{O}$  against the various org. acids is obtained. By transforming this into heat energy by multiplying by 23044 cal., the following figures for abs. affinities are obtained: benzoic acid 5346 cal., *o*-toluic 4839 cal., *m*-toluic 5277 cal., and *p*-toluic 5300 cal. Ostwald, who detd. the dissoc. consts. of the above acids by cond. measurements, obtained results at variance with the above, his consts. being: benzoic acid 0.00600, *o*-toluic 0.0120, *m*-toluic 0.00514, and *p*-toluic 0.00515. Therefore Ostwald judged *o*-toluic acid to be twice as strong as benzoic, although the figures based on abs. affinities show it to be considerably weaker. The abs. affinity of cinnamic acid for  $\text{Ag}_2\text{O}$  was also detd. by the same method and found to be 7305 cal., a value much higher than that for benzoic acid, whereas Ostwald found the dissoc. const. of this acid to be 0.00355, i. e., a little more than  $1/3$  that of benzoic acid. In investigating discrepancies between his detns. and published results, R. demonstrated the existence of 2 modifications of  $\text{Ag}_2\text{O}$ : (a) the electrolytically deposited variety, unstable at ordinary temp. but stable at higher temp., (b) the pptd. variety, stable at ordinary temp. but unstable at high temp. The transformation temp. was found to be  $132^\circ$  (by thermodynamic calcn.). The e.m.f. of the (a) variety in the element  $\text{Ag} \left| \text{Ag}_2\text{O}^{---} \right| \text{H}_2$  was found to be 1.177 as compared with 1.143 for the (b) variety. Another corollary of R.'s work is the calcn. of the e.m.f. of the element  $\text{H}_2 \left| \text{O}_2 \right.$  which is the sum of the e.m.fs. of the 2 elements (a)  $\text{Ag} \left| \text{Ag}_2\text{O}^{---} \right| \text{H}_2$  (1 atm.) and (b)  $\text{Ag} \left| \text{Ag}_2\text{O}^{---} \right| \text{O}_2$  (1 atm.). The e.m.f. of (a) is 1.177 v. The e.m.f. of (b) was calcd. to be 0.049 v., based upon Lewis' measurements of the dissoc. pressures of  $\text{Ag}_2\text{O}$  at higher temp., the extrapolated value for  $25^\circ$  being  $5 \times 10^{-4} \text{ atm.}$  (*Z. physik. Chem.* 55, 449 (1906)). Therefore, the e.m.f. of the element  $\text{H}_2 \left| \text{O}_2 \right.$  is  $1.177 + 0.049 = 1.226 \text{ v.}$ , a value which agrees well with the figure of 1.227 found by Brønsted (*C. A.* 3, 611 and *Z. physik. Chem.* 65, 744 (1909)) and 1.225 by Nernst and Wartenberg (*Z. physik. Chem.* 56, 544 (1906)). By the aid of R.'s methods, the *H-ion concn.*

may be detd. in cases where the ordinary H electrode cannot be used, e. g., in the presence of nitrates, nitro compds., unsatd. org. compds., etc. S. GULBRANDSEN

The rate of evaporation of a metal in a gas. SOPHUS WEBER. *Kgl. Danske Vidensk. Selskab. Math.-fys. Medd.* 3, No. 3, 16 pp. (1920).—Particular attention is given to the rate of evapn. of a heated W filament in a bulb filled with an inert gas ( $N_2$  or A). The treatment is entirely mathematical. Formulas are deduced for rate of evapn., taking into account various factors, such as the pressure and d. of the surrounding gas, the d. of the metal vapor, the diffusion const., also the nature and influence of the convection currents. The main result is that the rate of evapn. in any one gas is inversely proportional to the sq. root of the pressure of the surrounding gas, the temp. being kept const. This conclusion has been confirmed by the work of Oosterhuis (*Verh. XVI Med. Nat.-en Geneesk. Congres*, 1917, 101), who detd., the rates of evapn., at various pressures, of a heated W filament in an atm. of  $N_2$  and of A. If  $M_1$  represents the rate of evapn. in  $N_2$  and  $M_2$  in A, it was found that  $M_1\sqrt{p}$  was a const. at various pressures and was equal to 35, whereas  $M_2\sqrt{p}$  remained const. at 19.8 (the rate of evapn. being based on 100 in a vacuum and  $p$  being expressed in cm. Hg). The ratio between the rates of evapn. in A and  $N_2$  is therefore  $19.8/35 = 0.56$ , whereas the theoretical figure called for by W.'s mathematical deduction is 0.89. This discrepancy is attributed to the reaction between W and  $N_2$ , with the formation of the nitride  $WN_3$ . (Cf. Langmuir, *C. A.* 7, 3717.) S. GULBRANDSEN

Vapor pressure of binary mixtures. H. CASSEL. *Z. physik. Chem.* 101, 104-8 (1922).—A mathematical paper. It is emphasized that Dolezalek's theory regarding a special form of equation of state for pure gaseous, liquid or solid substances does not express a concrete assumption of any sort. H. JERMAIN CREIGHTON

Effect of pressure on the thermal conductivity of metals. P. W. BRIDGMAN. *Proc. Am. Acad. Arts Sci.* 57, 77-127 (1922).—Two methods are described for measuring the thermal cond. of metals under pressure. The first of these is a radial-flow method, which has many theoretical points of advantage, but is of limited applicability in practice because of the difficulty of getting metals in a condition of sufficient homogeneity. The second is a longitudinal-flow method, the essential of which is the small size of the specimen. The irregularities of the individual readings by the second method are greater than by the first method, but the effect of inhomogeneities is less and different specimens of the same metal give the same results. Measurements of the effect of pressures to 12000 kg./cm.<sup>2</sup> on the thermal cond. of Pb, Sn, Cd, Zn, Fe, Cu, Ag, Ni, Pt, Bi, and Sb have been made by one or the other of these methods. The effect may be either positive or negative, but is more often negative than positive. In only two cases, Pb and Sn, does the Wiedemann-Franz ratio increase under pressure; for the other metals it decreases and sometimes by large amounts. In addn. to the metals the pressure coeff. of thermal cond. of petroleum ether has been measured, the cond. increasing by a factor of about 2.2. These results indicate that a fairly large part of thermal conduction in a metal is performed by the atoms. Theoretical reasons are given for estg. the at. contribution to the thermal cond. as 50% of the electronic contribution. JAMES M. BELL

Consideration concerning the curves of cooling and heating. R. ARIANO. *Gazz. chim. Ital.* 52, I, 246-61 (1922).—The importance of cooling and heating curves in many phys. chem. and metallographic investigations makes an examn. of their theoretical behavior of interest, especially as to the influence of the dimensions of the specimens used to trace them and as to the appearance of the anomalies arising from the irregularity that occurs corresponding to the transformations that may take place in the material constituting the specimens. A. first examines the normal course (i. e., the cases in which no transformation occurs) of the curves: (1) time-temp. (equation  $T = \theta t$ ,

where  $\theta$  is time and  $T$  temp.); (2) temp.-difference between the substance being examd. and a control substance (equation  $T - T' = ft'$ , where  $T'$  represents the values of the magnitude corresponding to the control substance). The conclusions are stated in reference to the mathematical expressions developed in the test, except that it is stated that it is possible to apply Newton's law to the cooling curve of metallic specimens of small dimensions, without committing notable errors. A few exptl. results on Al are given; they confirm the theoretical conclusions. E. J. W.

**Fusion of carbon.** EUGEN RISHKEVICH. *Z. Elektrochem.* 27, 368-9(1921); cf. *C. A.* 15, 1432.—A criticism of statements made by Münch (cf. *C. A.* 15, 8235). The large current required by M. to fuse C was probably due to excessive cooling. M.'s failure to obtain more than a few drops of molten C is ascribed to the expts. probably being carried out in the open air. H. JERMAIN CREIGHTON

The specific heat of superheated steam for pressures from 20 to 30 atmospheres and from saturation temperature to 350°. O. KNOBLAUCH AND E. RAISCH. *Z. Ver. deut. Ing.* 66, 418-23(1922).—A more complete account of the work reported in *C. A.* 16, 1693. A still more complete account is promised in the *Mitteilungen über Forschungsarbeiten* of the Society. W. P. WHITE

The theory of specific heats near a change of state. E. BRODY. *Physik. Z.* 23, 197-9(1922).—Near the temp. where a change of state occurs deviations of single mols. from the mean mol. energy for that temp. are not equally probable upward and downward. Hence a correction term should be added to the usual theoretical formulas for the sp. heat. B. finds this correction term to be, for a solid near the m. p.:  $RT_s^2/MN(T_s - T)^2$ , where  $T_s$  is the m. p.,  $M$  the mass of the individual solid crystal,  $N$  the Loschmidt number. Very finely cryst. bodies should therefore show a greater increase of true sp. heat below the m. p. No numerical check is given, and actual observed variations are attributed mainly to impurities. W. P. WHITE

Determination of the upper inversion point of the specific heat of saturated benzene vapor. G. BRUBAT AND A. DELAYGUE. *Compt. rend.* 174, 937-9(1922).—By direct observation of the condensation under adiabatic expansions and compressions at various temps. it is found that the vapor condenses on compression below 258° and on expansion above that temp. Some expts. on the lower inversion point show also that it lies at about 122°. E. D. WILLIAMSON

The maximum heat of vaporization. E. ARIES. *Compt. rend.* 174, 1050-3(1922).—From the ordinary thermodynamic expressions for the sp. heats at satn. it can be shown that  $(dL/dT)$  is positive at zero abs. where  $L$  is the heat of vaporization. Since the heat must vanish at the crit. point it follows that it must have a max. somewhere between. E. D. WILLIAMSON

Condition equation of water. O. TUMLIRZ. *Sitz. Akad. Wiss., Wien, Abt. IIa* 130, 93-133(1921).—The following equation of state for  $H_2O$  has been developed:

$$[p + (B \times 10^{\frac{1}{4aT}})/v^2] (1 - \eta)/(1 + \eta) = (RT/v) (v + a)/(v - a),$$

where

$$\eta = \frac{A \left[ 1 - \lambda(t - \tau)10^{-\left(c - \frac{a\sqrt{(t+2t)^2 + 3t^2}}{6 + 8a\sqrt{t}}\right)t} \right] \sqrt{1 + 3/4a^2(x-a)^2} 10^{-\mu p(v + 3a\sqrt{x})(k - v)}}{v(V - b)\sqrt{T} \left[ 1 + \frac{(2 + 2at + 3aA p)p^{\frac{1}{2}}}{3a(v + a)T\sqrt{T}} \right]}$$

Here  $v$  is the volume of 1 kg. measured in m.<sup>3</sup>,  $p$  the pressure in mm. Hg,  $T$  the abs. temp.,  $t$  the temp. of the Centigrade scale. The consts. have the following values:  $R = 3.4620$  m.<sup>3</sup>/kg. mm. Hg,  $a = 0.00067759$  m.<sup>3</sup>/kg.,  $B = 3.4620$  m.<sup>3</sup>/kg. mm. Hg

$A = 1.223945 \cdot 10^{-4} \text{ m.}^2/\text{kg.}$ ,  $b = 0.000158956 \text{ m.}^2/\text{kg.}$ ,  $\lambda = 0.00021459 \text{ t.}$ ,  $t = 3.5092^\circ$ ,  $\alpha = 0.00067759$ ,  $c = 0.020725$ ,  $\mu = 0.0110444$ ,  $h = 362.8^\circ$ . The validity of the equation for  $\text{H}_2\text{O}$  in both the liquid and gaseous states has been verified with exptl. data. For liquid  $\text{H}_2\text{O}$  calcd. values for  $1000 \nu \text{ m.}^2/\text{kg.}$  agree closely with those detd. by expt. over a large range of pressures; while for  $\text{H}_2\text{O}$  vapor the calcd. pressure agrees closely with exptl. values. From the equation of state the expression  $P = [B \cdot 10^{1/4} a^7 / v^2] \cdot \{(1-\eta)/(1+\eta)\}$  is deduced for the cohesion pressure. It is shown that the occurrence of a max. d. for  $\text{H}_2\text{O}$  depends solely upon the manner in which the cohesion pressure depends on the temp.  $t$ . The quantity  $(1-\eta)/(1+\eta)$  decreases to a min. with increasing pressure and then increases.

H. JERMAIN CREIGHTON

**The  $25^\circ$  isotherms of the systems magnesium nitrate-sodium nitrate-water and magnesium sulfate-magnesium nitrate-water.** D. N. JACKMAN AND AGNES BROWNE. *J. Chem. Soc.* 121, 694-7(1922).—The quaternary system  $\text{Na-Mg-NO}_3\text{-SO}_4\text{-H}_2\text{O}$ , is of interest as it occurs naturally in the Chilean nitrate deposits. For its investigation a knowledge of the ternary systems  $\text{Na}_2\text{SO}_4\text{-MgSO}_4\text{-H}_2\text{O}$ ,  $\text{Na}_2\text{SO}_4\text{-NaNO}_3\text{-H}_2\text{O}$ ,  $\text{NaNO}_3\text{-Mg(NO}_3)_2\text{-H}_2\text{O}$ , and  $\text{Mg(NO}_3)_2\text{-MgSO}_4\text{-H}_2\text{O}$  is required. The first two have been published (Blasdale, *C. A.* 14, 1084; Massink, *C. A.* 11, 3184); the remaining two systems are herewith presented by use of 2 tables and 2 graphs. It is shown that at  $25^\circ$  no double salts or solid solns. are formed in either of these systems. J. T. R. ANDREWS

**Binary liquid mixtures.** O. FAUST. *Z. physik. Chem.* 101, 94-103(1922).—It is shown that for acetone- $\text{CHCl}_3$  mixts.,  $\pi/[P(\text{CH}_3)_2\text{CO} \cdot (1-X) + P_{\text{CHCl}_3} X] = cT$ , where  $\pi$  is the vapor pressure of the mixt.,  $P$  is the vapor pressure of the pure component at temp.  $T$ ,  $c$  is a const., and  $X$  and  $1-X$  are the mol. fractions of the components. The viscosity of binary mixts. can be calcd. by means of a similar rule of mixts. With acetone and  $\text{CHCl}_3$  the calcd. values agree closely with those detd. by expt. H. J. C.

**Binary liquid mixtures.** ALFRED SCHULZE. *Z. physik. Chem.* 101, 109-16(1922); cf. preceding abstract.—The vapor pressure of mixts. of  $\text{C}_6\text{H}_5\text{-CH}_2\text{CO}_2\text{CH}_3$ ,  $\text{C}_6\text{H}_5\text{-C}_2\text{H}_5$  and  $\text{C}_6\text{H}_5\text{-CH}_2\text{OH}$  has been calcd. at a no. of temps. by the rule of mixts. In most cases the calcd. results differ from the exptl. values by less than 2%. H. J. C.

**Equilibrium in the system ammonia-mercuric cyanide.** S. R. BRINKLEY. *J. Am. Chem. Soc.* 44, 1210-6(1922).—This system is studied at  $0^\circ$  by 2 methods (1) by vapor pressure measurements and (2) by soly. measurements. Between 369 and 1060 mm. the solid phase  $\text{Hg(CN)}_2 \cdot 2\text{NH}_3$  exists with vapor. At 1060 mm. a liquid phase appears, the liquid being a satd. soln. of this compd. in  $\text{NH}_3$ ; and above 1060 mm. there is unsatd. soln. and vapor only. The vapor pressures of these solns. are far below those required by Raoult's law. Soly. measurements in the presence of  $\text{H}_2\text{O}$  were possible because  $\text{Hg(CN)}_2$  forms no hydrates at  $0^\circ$ . The only solid phases were  $\text{Hg(CN)}_2$ ,  $\text{Hg(CN)}_2 \cdot \text{NH}_3$  and  $\text{Hg(CN)}_2 \cdot 2\text{NH}_3$ , as detd. by the method of residues.  $\text{Hg(CN)}_2$  would not be as suitable an adsorbent of  $\text{NH}_3$  as are  $\text{NH}_4\text{NO}_3$  and  $\text{NH}_4\text{CNS}$  because  $\text{Hg(CN)}_2$  is less sol. in  $\text{NH}_3$  and because the absorption of  $\text{NH}_3$  is much slower than by the other 2 salts. JAMES M. BELL

**The system silver perchlorate-water-benzene.** A. E. HILL. *J. Am. Chem. Soc.* 44, 1163-93(1922).—The system,  $\text{AgClO}_4\text{-H}_2\text{O}$ , has a eutectic point at  $-58.2^\circ$ , at which temp. the satd. soln. contains 73.9% of the salt. This is the lowest known eutectic for a true salt and  $\text{H}_2\text{O}$ . The soly. rises to 88.8% at  $99^\circ$ . The eutectic temp. of the system  $\text{AgClO}_4\text{-C}_6\text{H}_6$  is  $5.12^\circ$ , and the soln. contains 3.44% of the salt. The soly. curve rises steeply with the temp., almost reaching a perpendicular form between  $50^\circ$  and  $145^\circ$ ; at the latter temp. the satd. soln. contains 63.0% of the salt. The soly. curve resembles those where there are 2 liquid phases either in the stable or the metastable region. The hydrate  $\text{AgClO}_4 \cdot \text{H}_2\text{O}$  was isolated; its transition point is  $43.1^\circ$ ; the compd.  $\text{AgClO}_4 \cdot \text{C}_6\text{H}_6$  has a transition point at  $145^\circ$ ; the ternary system

$\text{AgClO}_4\text{-H}_2\text{O-C}_6\text{H}_6$  is marked by the possession of 6 realizable invariant equilibria, and a large number of monovariant equilibria, affording at least one example of every type of equil. theoretically possible for a ternary system contg. volatile components. The ternary eutectic representing 3 solid phases, soln. and vapor, is at  $-58.4^\circ$ ; the eutectic of the highest temp. is at  $42.1^\circ$ . The course of the 24 monovariant equilibria originating at these 2 quintuple points and the 4 intermediate quintuple points has been studied. Isothermal diagrams have been constructed to show the various equilibria existing at temps. between  $-58.4^\circ$  and  $145^\circ$ . Between  $5.24^\circ$  and  $22.4^\circ$  coexistent liquid phases can be prepd. in stable equil. with each other and their vapor. The occurrence of 2 sep. fields of unsatd. soln. is explained as due to the intersection of the soly. curve of  $\text{AgClO}_4$  with the binodal curve representing the limited soly. of  $\text{C}_6\text{H}_6$  and  $\text{H}_2\text{O}$ . The occurrence of a third field is explained as due to the existence, between  $-2.7$  and  $30^\circ$  approx., of an additional closed binodal curve, which does not extend to any one of the 2-component axes at any temp. It appears to be the first demonstrated case of a closed binodal curve.

JAMES M. BELL

**Equilibrium in liquid mixtures of ammonia and xylene.** C. A. KRAUS AND H. ZEITZUCHS. *J. Am. Chem. Soc.* **44**, 1249-60(1922).—The total vapor pressure of mixts. of  $\text{NH}_3$  and *m*-xylene has been detd. at a no. of temps. between  $8$  and  $20^\circ$  for the entire range of comps. The mixts. exhibit a crit. end-point at  $14.7^\circ$  at a pressure of 6.85 atm. and a compn. of 81.4 mol. %  $\text{NH}_3$ . The compn. of the liquid phases in equil. was detd. at the above temps. and at  $-33.5^\circ$ . The %  $\text{NH}_3$  in the phase rich in xylene decreases markedly with temp.

H. JERMAIN CRRIGHTON

**Effect of tension on the electrical resistance of certain abnormal metals.** P. W. BRIDGMAN. *Proc. Am. Acad. Arts Sci.* **57**, 41-66(1922); cf. *C. A.* **15**, 1447; **16**, 376.—The tension coeffs. of Li, Ca, Sr, Sb, Bi, manganin and therlo are detd. These substances are all abnormal in that their pressure coeffs. of resistance are positive. Young's modulus for these metals is also detd. The tension coeff. for Bi and Sr is found to be negative, but positive for the other five. The conduction mechanism of Li, Ca, Sb, manganin and therlo is on the whole transverse, that of Bi is longitudinal, and that of Sr is a combination. The negative tension coeff. found by Tomlinson (*Trans. Roy. Soc.* **174**, 1(1883)) for Ni is verified for Ni of high purity, and in addn., the hysteresis effects and the effect of changes of temp. are studied. Co, on the other hand, is entirely normal. It is suggested that the explanation for the abnormal behavior of Ni may be found in a depression by tension of the transition point normally at  $380^\circ$ .

JAMES M. BELL

**Failure of Ohm's law in gold and silver at high current densities.** P. W. BRIDGMAN. *Proc. Am. Acad. Arts Sci.* **57**, 131-72(1922); cf. *C. A.* **16**, 2063.—By the employment of a new method, by which the resistance is measured simultaneously for a heavy d. c. and a small superimposed a. c. of acoustical frequency, deviations from Ohm's law at high current densities are detected and measured in leaf Au and Ag. The maximum current densities were about  $5 \times 10^6$  amp./cm<sup>2</sup>, and the deviations from Ohm's law were of the order of 1%. If the mechanism of conduction is a free path mechanism, these results probably mean that the free path is much longer than supposed on the classical electron theory.

JAMES M. BELL

**Rapid electrolysis without rotating electrodes.** GRAHAM EDGAR AND R. B. PURDUM. *J. Am. Chem. Soc.* **44**, 1267-70(1922).—The app. consists of a simple glass vessel to which are sealed 3 glass "air lifts" connecting in a single tube at the bottom and entering symmetrically about half way up the main vessel, the upper seals being made tangentially. Stirring by this method gives results for the pptn. of Cu which compare favorably with those obtained with rotating electrodes.

JAMES M. BELL

**Further studies on dielectric hysteresis and allied phenomena.** I. H. SARGENT.

*Sci. Repts. Tohoku Imp. Univ.* 10, 437-43(1921).—Two kinds of hysteresis are distinguished, plastic and stationary. The stationary hysteresis loop in quartz is easily distinguished from the plastic hysteresis loop both by its form and magnitude. For crystals of the monoclinic type, the time effect, residual charge and hysteresis are much smaller than those of crystals belonging to the hexagonal and isometric type. The value of the limit potential in the case of the former crystal is very large compared with that of the latter. A dielectric having a large time effect and residual charge also shows a large hysteresis loop. The form of the hysteresis loop is characteristic for different crystals and for different directions of the same crystal. The impurities in a crystal greatly magnify its hysteresis and allied phenomena, and depress the value of the limit potential.

E. F. PERKINS

**The quantum theory of dielectrics.** H. SARGUSA. *Sci. Repts. Tohoku Imp. Univ.* 10, 445-52(1921).—The mathematical expression is deduced for the dielec. const. based on the 2nd hypothesis of Planck's quantum theory, taking into account Sommerfeld's integral phase. Theoretical results give the variation of dielec. const. with respect to temp. and this also agrees with the exptl. results.

E. F. PERKINS

**Relations between molecular refraction and other properties.** W. HERZ. *Z. physik. Chem.* 101, 54-62(1922).—The mol. vol. at the b. p. is 5 times greater than the mol. refraction. This relation can be used to calc. mol. wt., the diam. of mols. and internal pressure. In many instances the quotient of the mol. heat of vaporization at the b. p. and the mol. refraction is approx. 8 times the value of the crit. pressure. The following relation exists between the coeff. of expansion ( $k$ ), the mol. refraction ( $MR$ ) and the crit. pressure ( $p_c$ ):  $MR \cdot p_c / (k_{20} + 293) = \text{const. (0.9)}$ .

H. J. C.

**The thermel.** W. P. WHITE. *Science* 55, 617-8(1922).—The classical names, thermocouple and thermopile, are awkward when applied to temp.-measuring instruments, which frequently include both at once, and where the mere number of parts is usually a secondary matter. A single term for all such instruments is desirable. The term "thermoelectric thermometer" is logical, but unnecessarily long; "thermoelement" is not logical, and its use has caused considerable confusion. The term "thermel," which is merely an abbreviation of "thermoelectric thermometer," is logical, short and definite, has met with general informal approval, and is urged as a desirable general term for all thermoelec. temp.-measuring devices. "Thermocouple" and "multiple thermel" (or "thermopile") may still be used in the few cases where it is desirable to call attention to the special construction of the thermel.

W. P. WHITE

Electrical charges of colloidal particles and anomalous osmosis (LOBB) 11A. The colloidal behavior of edestin (HITCHCOCK) 11A. A contribution to the theory of solid solutions, mix-crystal formation and isomorphism (JAKOB) 8. Determination of the density of W (BURGER) 3. Use of the oxides of platinum for the catalytic reduction of organic compounds (VOORHEES, ADAMS) 10.

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### 3—SUBATOMIC PHENOMENA AND RADIOCHEMISTRY

S. C. LIND

Modern ideas on the elements and on the structure of atoms. H. OLLIVIER. *Bull. soc. ind. Mulhouse* 88, 126-48(1922).—A review. A. P.-C.

Modern theories on the constitution of matter. R. DELABY AND R. CHARONNAT. *Bull. sci. pharmacol.* 29, 191-213, 267-80(1922).—A review. F. S. HAMMETT

Radioactivity and atomic constitution. LISE MEYNER. *Naturwissenschaften* 9, 423-7(1921).—See *C. A.* 16, 2067. H. G.

Atoms and molecules. II. ALBERT C. CREHORE. *Phil. Mag.* 43, 886-914 (1922); cf. *C. A.* 16, 377.—In part I of the present paper a concrete picture with diagrams is presented of the forms of atoms from H to Na inclusive (including isotopes) which conform with the Saha electromagnetic theory. The electron is described as an oblate spheroid with axes about 3-1. The distance from the center of the N atom to the H in N is just 2 diams. of the electron, in agreement with Rutherford. General formulas (not given) have been developed to test the atomic forms proposed by means of the known chem. combinations of atoms to form mols. In part II, the shape of the negative electron is considered as a most important factor in detg. the equil. distances between 2 atoms forming a mol. The approx. const. distance between the centers of atoms in all solids is directly connected with the shape of the electron and for this reason is a universal distance. In order for the atoms to unite at all, the eccentricity of the electron must be

between about 0.9 and 1.0, in agreement with 0.945 deduced in the first paper from an entirely different assumption. It is shown that He and Ne atoms will not form compds. and must be monatomic. The exact detn. of some of the simpler mols. is deferred to a later paper.

S. C. LIND

**A magnetic model of atomic constitution.** J. K. MARSH AND A. W. STEWART. *Nature* 109, 340(1922).—Equal magnets ( $n$  in number) are fixed vertically at the bottom of a lead tank filled with water, above the surface of which  $n$  other equal magnets are held in a glass tube. A third set of  $n$  magnets float on cork disks. All have their north poles up. The floating magnets in general arrange themselves in 2 groups, one of which is central and is called the nucleus. With  $n = 1, 4, 6, 7, 9, 10, 11$ , etc., the numbers in the 2 groups are 1 and 0, 2 and 2, 3 and 3, 4 and 3, 5 and 4, 5 and 5, 6 and 5. Attention is called to the analogy with the usual proton-electron models for light atoms. Here, except in the case of H, the no. of magnets not in the nucleus represents the at. no. of an atom species of wt.  $n$ . This correspondence holds as far as  $n = 20$ . The cases  $n = 2, 3, 5$  and 8 are also described. Some chem. significance is ascribed to similarities in the arrangements in the case of  $n = 11$  (boron) and 12 (carbon).

NORRIS F. HALL

**Experimental proof for "Richtungs Quantelung" in the magnetic field and magnetic moment of a silver atom.** WALTER GERLACH. *Physica* 2, 122(1922).—Confirming his exptl. theoretical deductions with Stern (*C. A.* 16, 1179), G. has found that a ray of Ag atoms is split in a magnetic field into two distinct rays. A radiation consisting of Ag atoms is produced by heating the metal to white heat. The normal Ag atom in the gaseous state has one single quantum, its magnetic moment being equal to the magneton of Bohr.

R. BRUTNER

**An attempt to detect induced radioactivity resulting from alpha-ray bombardment.** A. G. SHENSTONE. *Phil. Mag.* 43, 938-43(1922).—An attempt attended with negative results to detect the emission of particles from atomic residues immediately following their disturbance by the emission of H or He particles under  $\alpha$ -ray bombardment. By placing the material under examn. on the dial of a wheel rotating at high velocity, the interval of time elapsing between bombardment and observation was made very short. The conclusion drawn from the absence of scintillations is that in the cases of Al, C, and Fe no mass particles of range greater than 2 mm. are produced after an interval of  $8 \times 10^{-4}$  sec. and none of range greater than 6 mm. after  $3.3 \times 10^{-4}$  sec. For Pb the corresponding intervals are  $1.2 \times 10^{-4}$  and  $5.0 \times 10^{-4}$  sec.

S. C. LIND

**Radium production in America.** S. C. LIND. *Chem. Met. Eng.* 26, 1012-3(1922).—Comment is made upon the articles of d'Aguiar on Ra extrn. (*C. A.* 16, 680). Their appearance is commended, but certain statements made by d'Aguiar require modifications. These are discussed by L.

D. C. BARDWELL

**The question of the existence of a new radioactive element U V described by Piccard and Stahel.** OTTO HAHN. *Physik. Z.* 23, 146-53(1922).—The activities of a number of UX preps. were studied over a period of 8 months. Correcting for small quantities of UX<sub>1</sub> present, the period of half life of the preps. coincides with that for UX (24.5 days). There is no evidence for the existence of a new radioactive element (period of half-life of 48 days) described by Piccard and Stahel. (*C. A.* 16, 2068).

D. C. BARDWELL

**The occurrence of ionization by cumulative effects.** FRANK HORTON AND ANN C. DAVIS. *Phil. Mag.* 43, 1020-3(1922).—Reply to Compton (*C. A.* 16, 2070).

S. C. L.

**The disappearance of gas in the electric charge. IV. THE RESEARCH STAFF OF THE GENERAL ELECTRIC COMPANY, LTD., London.** (Work conducted by N. R. CAMPBELL AND H. WARD.) *Phil. Mag.* 43, 914-37(1922); cf. 15, 466, 2779, 3030.—

A continuation of work on the disappearance of gases in discharge tubes under various conditions, especially with reference to the enhanced absorption in the presence of  $\text{I}$  and other substances. Compound gases have been excluded as subject to chem. change. The inert gases are little adsorbed.  $\text{H}$  and  $\text{N}$  which have been used in all other expts. behave approx. identically. The nature of the discharge has little influence. The form of the vessel is important only in affecting the wall area exposed to discharge. Temps. around  $20^\circ$  are without effect. Pressure of the gas during adsorption has no effect within wide limits on the amt. adsorbed. Adsorption increases with the amt. of  $\text{P}$  introduced. The state of the glass wall has little influence but the adsorptive power is greatly increased by "evapg." certain substances ( $\text{W}$  and other metals which may be regarded as substituting  $\text{P}$ ) from a heated filament. The ionization of the vapor is an important factor. In the absence of  $\text{P}$  adsorption is indeterminate, balancing between true adsorption and liberation. The absorption of gas when mixed with  $\text{P}$  vapor occurs in 2 stages, rapid during deposition of  $\text{P}$ , and slow after deposition. Adsorption appears to be detd. only by ionization and will take place slowly even in the absence of glow. There is no lower limit to the pressure due to adsorption. The gas is again liberated on evapg.  $\text{P}$  from the walls. Compds. such as  $\text{PH}_3$  have been demonstrated, but are secondary in importance. As acts similarly to  $\text{P}$ . A theory is put forward involving polar layers on the wall or deposited substances, to which ions adhere in virtue of their charges. Probably it is the negative ion which adheres. S. C. L.

**The electrodeless discharge in certain vapors.** J. K. ROBERTSON. *Phys. Rev.* 19, 470-7 (1922); cf. C. A. 15, 2349.—K at  $250\text{--}300^\circ$  gave a bright ring with several members of each subordinate series.  $\text{Li}$  gave a slight glow up to  $500^\circ$  due to impurities. In  $\text{Hg}$  indications of polyatomic mols. were obtained. In  $\text{I}$  between  $-5^\circ$  and  $+5^\circ$  a pale yellow ring changed to a green, pink-bordered ring with line spectrum which was thought to be due to atoms of iodine. The application of this tube to the study of the spectra of isotopes with the aid of an instrument of high dispersion is pointed out. F. O. A.

**The pressure of radiation in transparent dielectrics.** SATYENDRA RAY. *Phys. Rev.* 19, 467-9 (1922).—To explain the negative *photophoresis* observed by Ehrenhaft (C. A. 14, 1258), if the ether has an elec. density and magnetic density other than zero then the relative motion of one dielectric immersed in another would be due to the difference between these radiation forces per unit vol. (cf. C. A. 15, 1101). F. O. A.

**The reflection of X-rays from imperfect crystals.** C. G. DARWIN. *Phil. Mag.* 43, 800-20 (1922).—A theoretical inquiry into the possibility of detg. the arrangement of electrons in atoms from the intensity of X-ray scattering. The problem is divided into 2 stages, from crystal to mol., and from mol. to electrons. Only the first is treated. The difficulty of dealing with "extinction" was encountered by Bragg, James and Bosanquet (C. A. 15, 2786). D. distinguishes 2 classes of extinction, primary and secondary, only the latter being eliminated by the simpler treatment of B., J. and B. D.'s theoretical results are compared with the exptl.; the agreement is not very good, probably owing to inadequate exptl. data. S. C. L.

**Diffraction of Röntgen rays.** W. H. KRESOM. *Physica* 2, 118 (1922).—The diffraction is measured by the method of Debye and Scherrer; the liquids which are to be examd. are contained in a vessel of glass or  $\text{Al}$  in a thin layer. By measuring half the top angle of the cone formed by the Röntgen-rays, the following values were obtained:  $\text{O}_2$   $27^\circ$ ,  $\text{A}$   $27^\circ$ ,  $\text{C}_6\text{H}_6$   $18^\circ$ ,  $\text{H}_2\text{O}$   $29^\circ$ ,  $\text{C}_2\text{H}_5\text{OH}$   $22^\circ$ ,  $(\text{C}_2\text{H}_5)_2\text{O}$   $19^\circ$ . K. maintains that the diffraction is exclusively due to the action of neighbouring mols., not to atoms inside the mol. Some liquids—like  $\text{H}_2\text{O}$ —which contain groups in which the mols. have a smaller distance from each other exhibit peculiar figures with a double ring. R. BRUNNER.

**Determination of density of tungsten by means of Röntgen-rays.** H. C. BURTON. *Physica* 2, 114 (1922).—Direct detn. of the d. of solid substances furnishes unsatisfactory

results, especially so with metals where very variable values are obtained. It is evident that this is due to cavities in the metal as the  $d$ . seems to increase through mech. treatments such as hammering or drawing to wires. B. det. the ratio of the  $d$ . of NaCl and the  $d$ . of W by photographing the Röntgen-spectrum of a mixt. of those two substances according to the method of Debye and Scherrer. He measures, in this way, the angles of deflection of any of the two neighbouring rays which correspond to NaCl and to W, resp. Let  $T$  be one such angle for W,  $\Delta$  the distance of two neighboring strips of NaCl and of W and  $R$  the radius of the film, then the ratio of the elementary cubes of NaCl and W equals:  $\sin^3 [(T/2) + (\Delta/(2R)) : \sin^3 (T/2)$ . If this value is multiplied by the ratio of the mol. wts. of NaCl and W and divided by 2 the looked for ratio of the  $d$ . of NaCl and W is obtained. This is equal to 8.96. As the  $d$ . of NaCl equals 2.164 it follows that the  $d$ . of W is 19.37.

R. BEUTNER

Observations and experiments on the occurrence of spark lines (enhanced lines) in the arc. II. Magnesium, zinc and cadmium. G. A. HEMSALECH AND A. DE GRAMONT. *Phil. Mag.* 43, 834-71(1922); cf. C. A. 15, 3790; 16, 1363.—Detailed results are given of observations of the spectra of Mg, Zn and Cd under various arc conditions. Photographic records show the relative behavior and the characteristic features of various types of lines. The emission of spark lines during the first phase of a liquid film arc is independent of the nature of the liquid which does not play the role of a dielectric since electrolytes act in the same way. Many other arc phenomena of the 3 metals are fully discussed.

S. C. L.

The appearance of unsymmetrical components in the Stark effect. A. M. MOSHARFA. *Phil. Mag.* 43, 943-52(1922).—A mathematical treatment of the Stark effect which predicts that in high elec. fields the distribution of the components produced would no longer be symmetrical about the original line according to the present theory. An investigation using higher fields than yet employed is suggested as a test of the fundamental hypothesis of the quantum theory of spectra.

S. C. L.

Recent applications of the spectroscope. S. J. LEWIS. *Chemist and Druggist* 94, 836-90(1921).—An abstr. of 3 lectures.

S. WALDBOTT

Structure of organic compounds (BRAGG) 10.

#### 4—ELECTROCHEMISTRY

COLIN G. FINK

Thomas Duncan. ANON. *Elec. World* 80, 2(1922); 1 illus.—Biographical sketch.

C. G. F.

Electrochemistry. K. ARNDT. *Fortschritte Chem.* 16, 129-49(1921).—Progress in 1915-9.

C. C. DAVIS

Regenerative car furnace. A. D. DAUCH. *Iron Age* 109, 1217-8(1922).—A 3-chambered regenerative car-type elec. furnace is used for annealing  $\frac{1}{8}$ -in. diam. wire in coils of 250 lb. each. One chamber is designed for heating, one for cooling and one for preheating. Ni-Cr ribbon elec. heating units are installed in the heating chamber only. A cold charge is placed in the preheating chamber which has its full side opening into the cooling chamber. After 3 hrs. the preheated charge is transferred to the heating chamber where it remains another 3 hrs. It is then run into the cooling chamber to transfer its heat to a fresh cold charge. The furnace delivers 7,500 lb. of annealed wire every 3 hrs. For a 10-hr. day the power consumption per ton of product is 185 kw. hrs.; for a 24-hr. day it is not in excess of 115 kw. hrs.

LOUIS JORDAN

The manufacture of cyanogen compounds in Canada. H. FREEMAN. *Can. Chem. Met.* 6, 129-31(1922); cf. C. A. 16, 1379.—F. traces the development of the manuf.

of CN compds. by the elec. furnace process yielding a product contg. up to 86% CN, calcd. as NaCN. Raw lime-N, rock salt, and powd.  $\text{CaC}_2$  are fed into large crucible-shaped elec. furnaces, lined with C blocks. A single graphite electrode 12" (30 mm.) in diam. extends to within 12" of the bottom of the furnace. The bottom is also electrically connected and single phase current is used. High c. d. is employed insuring very rapid melting between the end of the electrode and the furnace bottom. When the current reaches the fixed upper limit corresponding to a known temp. of the fused cyanide, the plug in the tap hole in the bottom of the furnace is withdrawn. The fused material flows down a conduit to a sump and is rapidly cooled from about 1350° to a black heat by means of a rotating water-cooled wheel. The material is removed in the form of thin flakes by a scraper and packed in sheet iron or steel drums. After a batch has been tapped the superimposed layer of partially heated material falls down and the process continues without elec. contact-breaking. F. contends that the CN exists as NaCN and gives tests bearing out his contention. W. H. BOYNTON

**Experiments on the bell type of electrolytic soda apparatus.** MATSUCHI YASUDA. *J. Chem. Ind. (Japan)* 24, 1006-22(1921).—A small porcelain box is set up in an inclined position (12° to the horizontal). A small Fe plate is the cathode. Six figures are given to show the detailed construction. Using 3 amps./10 cm.<sup>2</sup> of horizontal cross section of the bell, at 4 v. or more, Y. obtained 135 g. of NaOH per l. With 24 cells, 110 v. and 120 amp. and 59 days, the following results were obtained: current yield 84%, energy for 1 kg. NaOH, 3.73 kw. hr. and concn. of NaOH, 130.78 g. per l. C anodes and NaCl as electrolyte are used. Full details are tabulated. S. T.

**Electrolytic extraction of zinc.** L. CAMBI. *Giorn. chim. ind. applicata* 4, 133-47 (1921).—Descriptive and critical. The topics comprized are: national conditions with regard to Zn metallurgy; present development of hydroelectrometallurgy of Zn;  $\text{ZnSO}_4$  electrolytic process; national development of Zn electrometallurgy. Photographs and diagrams are given. ROBERT S. POSMONTIER

**Storage battery plates using the scaly lead powder electrolytically deposited as the active material.** HIROMU TANAKA. *J. Chem. Ind. (Japan)* 24, 995-1005(1921).—Scaly Pb powder was prepd. as follows:  $\text{Pb}(\text{NO}_3)_2$  soln. contg. a little AcOH was electrolyzed, Pb being used as electrodes. The product collected from the cathode was washed with  $\text{H}_2\text{O}$ , and dried quickly on a heated Al plate. The powder obtained was pasted with  $\text{H}_2\text{O}$ , NaOH,  $(\text{NH}_4)_2\text{SO}_4$  or  $\text{MgSO}_4$  and after thoroughly drying was fixed in dil.  $\text{H}_2\text{SO}_4$ . Automobile storage battery plates were made 12 cm.  $\times$  14 cm.  $\times$  3.5 mm. in size, 800 cc. of  $\text{H}_2\text{SO}_4$  (d. 1.210 at 18°) being used. The battery was alternately charged (4.2 amps.) and discharged (4. amp.) every 3 hrs., 64 times. Expts. were conducted mainly with the anode to det. capacity of plates and its relationship to size of scale, pasting materials and porosity of the paste. The results show that the finer the powder, the greater the capacity. Even such sizes, which are very unsatisfactory if non-scaly Pb powder is used, gave fairly large capacity, probably due to porosity of the scaly powder. The pasting liquid is not as important as the size of the powder. In general,  $\text{MgSO}_4$ ,  $\text{H}_2\text{O}$  or caustic are most satisfactory. Porosity is detd. by the amt. of  $\text{H}_2\text{O}$  the plate will hold. The coarse powders give higher capacity at first, but the finer powders show greater durability. Therefore, the finer powders are to be preferred, 160 mesh being the most satisfactory size. Plates made with the scaly Pb powder, electrically deposited, make a far better battery than is now on the market. S. T.

**Measuring direct current with split core transformer.** G. I. HILL. *Elec. World* 80, 24(1922). C. G. F.

Reducing and oxidizing action of alternating currents (COLLENSBERG, BODVORSS)  
2. Rate of evaporation of a metal in a gas (WÄGER) 2. Cathodic reduction of elementary N (FICHTER, SUTTER) 2.

KREMMANN, R.: *Elektrochemische Metallkunde*. Vol. II. 1st Pt. 3rd Sect. of *Metallographie* (cf. Guertler, C. A. 16, 1206). Berlin: Gebrueder Borntraeger. 656 pp. \$10.50. Reviewed in *J. Am. Chem. Soc.* 44, 1161(1922).

**Storage batteries.** H. M. WILLIAMS. U. S. 1,417,007, May 23. Pb plate batteries with a solid electrolyte are prepd. by charging and discharging the plates in  $H_2SO_4$  of ordinary battery strength until the acid in the pores of the plates is of about 1.2 sp. gr., then removing the free electrolyte and substituting a mixt. of "liquid Na silicate" 1,  $H_2O$  3 and  $H_2SO_4$  (d. 1.4) 5 parts. This mixt. reacts to form a voluminous mass contg. colloidal  $SiO_2$ .

**Storage battery.** J. C. SUNDBY. U. S. 1,417,214, May 23. Structural features.

**Storage battery plates.** F. BRUCE. Can. 219,258, June 6, 1922.

**Separators for storage batteries.** G. STIERUP. U. S. 1,416,761, May 23. Separator material is prepd. by elec. fusion of a mixt. of conducting and non-conducting material contg. a gas-forming substance, e. g., kieselguhr, Fe or Cu and a binder such as pitch or paraffin.

**Paste for storage plates.** T. A. WILLARD. Can. 219,532, June 13, 1922. A small amt. of wood dust is mixed with the active material to keep up the capacity of plates employed in storage batteries. Cf. C. A. 15, 1658.

**Lead paste for storage battery plates.** C. C. CARPENTER. U. S. 1,416,787, May 23. Sponge Pb is ground and mixed with  $H_2SO_4$ . U. S. 1,416,788 relates to structural features of storage battery plates.

**Secondary batteries.** F. J. HOLMES. Can. 218,487, May 9, 1922.

**Galvanic cells.** R. SCHUSTER. Can. 219,929, June 20, 1922. A perforated standpipe is placed in the catholyte of the cell for the elimination of decompn. products. Cf. C. A. 15, 2037.

**Dry-cell electric battery.** H. F. FRENCH. U. S. 1,416,704, May 23. Structural features.

**Negative electrodes for accumulators.** A. POUCHAIN. Can. 218,384, May 9, 1922. The electrode consists of a thin plate of metal which is a good conductor and which is not attacked by the electrolyte, and a number of Zn pieces interlaced with the plate.

**Electrolytic spray-coating or lettering.** W. E. BAILLY. U. S. 1,416,929, May 23. An electrolyte such as  $CuSO_4$  soln. is projected against a plate of metal to be coated which forms one electrode and the spray nozzle forms the other electrode.

**Battery electrolyte.** A. L. MUREN. U. S. 1,416,738, May 23. Alk. electrolytes such as those used with Zn and Ni hydroxide are prepd. with a tungstate, e. g., Na or K tungstate, which prevents "treeing" and short-circuiting.

**Electrolyzer of the tank type.** R. PECHERANZ. Can. 219,504, June 13, 1922.

**Electrolytic tanks with diaphragm cells.** G. HUGLUND. Can. 219,587, June 13, 1922. An electrolytic tank having a diaphragm cell has a tube with one end in the diaphragm cell, the other being pressed against an opening in the wall of the tank. Means are provided for regulating the level of liquid in the cell.

**Electrolytic cells for hydrogen and oxygen generation.** JNO. HARRIS. Can. 219,590, June 13, 1922. Structural features.

**Electrolytic apparatus for hydrogen and oxygen manufacture.** C. G. SPENCER. Can. 219,645, June 13, 1922. Structural features.

**Apparatus for electric production of ozone.** H. E. ELLIS. U. S. 1,417,046, May 23.

**Electrolytic apparatus for extracting metal from ores.** H. H. GODFREY. Can. 219,494, June 13, 1922.

**Recovering copper from its ores.** C. J. A. DALZIEL. Can. 219,866, June 20, 1922. Finely crushed ore and an acid soln. are fed into a preparatory vessel where a pulp

is formed by pneumatic agitation; the pulp is passed through a series of electrolytic cells where sedimentation is prevented by the introduction of a blast of air at the bottom of each cell and the barren pulp is discharged from the last cell.

**Obtaining of gold or silver from their ores.** A. A. LOCKWOOD. Can. 218,617, May 23, 1922. Finely divided ore is agitated in cyanide liquor and a continuous stream of the pulp is fed through an electrolytic cell through which a current is passing, the pulp being held in suspension by means of a jet of air. The pulp is returned to the cyaniding tower and the operation repeated without filtering the pulp.

**Electrolytic production of iron laminae.** C. DANTSIZEN. U. S. 1,416,692, May 23, 1922. A rotating W cathode is used which is partially submerged in the electrolyte and from which the deposit is continuously stripped.

**Nitrogen compounds with oxygen.** A. C. CLASSEN. Can. 219,857, June 20, 1922. Air is subjected to the simultaneous action of elec. dark discharges and spark discharges at 50-90° in the presence of colloidal metal compds. as contact substances.

**Chromic acid regeneration.** R. H. MCKEE. Can. 219,176, May 30, 1922. Solns. contg. salts of Cr are oxidized by establishing a definite flow of the soln. past opposed anode and cathode surfaces sepd. by a porous diaphragm and passing a current between the electrodes. Cf. C. A. 16, 1541.

**The production of plates and sheets by electrodeposition.** S. O. COWPER-COLLS. Can. 219,577, June 13, 1922. Structural features of a matrix-holding frame.

**Electrolytic production of metal foil.** T. A. EDISON. U. S. 1,417,464, May 23, 1922. Metal such as Ni is deposited upon a partially submerged rotating drum electrode and the deposited film is continuously stripped from the drum outside the electrolyte.

**Cleaning metals by electrolysis.** I. R. JASCOWITZ. Can. 219,629, June 13, 1922. The metal article is immersed as cathode in an electrolyte of spent caustic melt soln. contg. NaOH 50, Na<sub>2</sub>SO<sub>4</sub> 28, Na<sub>2</sub>SO<sub>3</sub> 8, Na<sub>2</sub>CO<sub>3</sub> 8 and phenol 1-2%.

**Cleaning articles electrolytically.** E. L. COUCH. Can. 218,335, May 9, 1922. A metal article is placed upon an electrode, both electrodes are kept in motion and an electrolyte is directed against the electrodes.

**Coloring metals electrolytically.** T. RONDELLI and Q. SESTINI. U. S. 1,417,413, May 23, 1922. Metals such as Fe, Cu or brass are colored by anodic oxidation in a soln. of an alk. electrolyte contg. Cu. Cf. C. A. 16, 28.

**Electrical precipitation of suspended particles from gases.** E. R. WOLCOTT. U. S. 1,416,769, May 23, 1922. Before pptn. by the action of an a. c., gases such as cement kiln or smelter gases are humidified to facilitate the pptn. of suspended particles from them.

**Apparatus for the electrical treatment of gases.** E. R. WOLCOTT. Can. 218,490, May 9, 1922. Discharge electrodes alternate with collecting electrodes in a flue and both are kept at a high potential difference while gases pass through the flue and through the electrodes which extend transversely in the flue.

**Electric furnaces.** M. SAUVAGEON. Can. 219,805, June 20, 1922. A resistance furnace heating by radiation through the crown has the space above the crown filled with a resistance material. The crown and walls of the furnace are composed of a good conductor of heat which becomes an electric conductor at high temp.

**Tilting electric furnace.** W. DYKSEN. U. S. 1,416,699, May 23, 1922.

**Electrode furnaces.** W. DYKSEN. Can. 219,975, June 20, 1922. The electrodes are arranged in the furnace in a common counterbalanced system, one counterbalancing another.

**Electric furnace adapted for refining metals.** H. DE NOLLY. U. S. 1,417,303, May 23, 1922.

**Electric furnace regulator systems.** C. A. BODDIS. Can. 219,624, June 13, 1922. The system has an electromagnet controlled in accordance with the current of

the two poles, second magnet controlled in accordance with the voltage across the arc, both magnets cooperating to govern the same contact members which govern reversing switches for an electrode motor. The reversing switches govern elements for varying the energization of the electromagnets in order to prevent hunting action. Means are also provided for establishing a dynamic braking circuit for the electrode motor.

**Electric furnace regulator system.** C. A. BODDIE. Can. 219,625, June 13, 1922. The system comprises an adjustable electrode operated by a motor, switches for controlling the direction of rotation of the motor, a main control electromagnet operated in accordance with the current passing through the furnace for selectively operating the switches and means controlled by the switches for directly varying the energization of the main control magnet in accordance with the switch operated.

**Induction furnace having uni-directional circulation.** J. R. WYATT. Can. 219,098. Beneath the furnace chamber and connected therewith is a resistor channel, of restricted cross section in one part, for molten metal, in combination with an a. c. transformer having one leg threaded through the channel. The leg is nearer the metal at the more constricted part of the channel than other parts thereof.

**Metallic filaments for incandescent electric lamps.** K. NISHIMOTO. Can. 218,833, May 23, 1922. A mixt. of W with 0.2 to 1.0% of Th is pressed into the form of sticks and given a preliminary heat in the mold. The sticks are then heated to near the m. p. by passing an elec. current through them, slowly cooled to a dull red, hammered or rolled at this temp. until they become ductile and finally drawn to produce filaments.

## 6—INORGANIC CHEMISTRY

H. I. SCHLESINGER

The process " $\text{NH}_4\text{COONH}_4 + \text{H}_2\text{O} = (\text{NH}_4)_2\text{CO}_3$ " and " $\text{CO}_2 + \text{H}_2\text{O} = \text{H}_2\text{CO}_3$ ". C. FAHRMOT. *Z. anorg. allgem. Chem.* 120, 85–102 (1921).—If a soln. contg.  $\text{CO}_2$  and  $\text{H}_2\text{CO}_3$  is quickly added to a strong  $\text{NH}_3$  soln., the free  $\text{CO}_2$  present unites quantitatively with the  $\text{NH}_3$  forming ammonium carbamate. So stable is the carbamate thus formed that the addn. of  $\text{BaCl}_2$  will, without affecting the carbamate, quantitatively ppt. the  $\text{H}_2\text{CO}_3$ , as  $\text{BaCO}_3$ , which may be removed by filtration. The ionization const. of carbonic acid is  $10^{-4.3}$  at  $0^\circ$ . The rate of hydration of  $\text{CO}_2$  was most rapid in  $\text{NaOH}$  soln., decreasing irregularly as the H-ion concn. increased. In investigating the process  $\text{NH}_4\text{COONH}_4 + \text{H}_2\text{O} = (\text{NH}_4)_2\text{CO}_3$ , the initial concn. of ammonium carbamate was usually 0.02 *M*. Temp. was mainly  $0^\circ$ . Even in very weakly acid solns. complete decompn. of the carbamate was nearly instantaneous. In 0.1 *N*  $\text{NaOH}$  soln. at  $18^\circ$ , the carbamate (0.05 *M*) was completely decompd. in 3 days. In 1.0 *N*  $\text{NaOH}$  soln. at  $0^\circ$  a month was required for complete decompn. The reaction was seemingly monomol. When the solvent was water or contained  $\text{NH}_3$  or  $\text{NH}_4\text{Cl}$  the action goes to equil. Increasing the concn. of either one or both of  $\text{NH}_3$  or  $\text{NH}_4\text{Cl}$  displaces the equil. to the left.  $\text{NaCl}$  has a similar effect. Equil. consts. obtained varied from 0.32 to 0.41. Velocity consts. varied from 0.006 to 0.059. J. C.

**Attempts to prepare pure calcium cyanide.** HEINRICH PINCASS. *Chem. Ztg.* 46, 347 (1922).—The method of Schulz (*J. prakt. Chem.* 68, (1856)) gave  $\text{Ca}(\text{OH})_2$  and 10% of  $\text{Ca}(\text{CN})_2$ ; that of Joannis (*Ann. chim. phys.* [5] 26, 496 (1882)) in aq. soln. gave solids contg. up to 33%  $\text{Ca}(\text{CN})_2$ . Dry  $\text{HCN}$  over  $\text{CaO}$  at room temp. gave  $3\text{Ca}(\text{OH})_2 \cdot 2\text{Ca}(\text{CN})_2 \cdot 13\text{H}_2\text{O}$  ( $\text{Ca}(\text{CN})_2 = 41\%$ ); at  $600\text{--}700^\circ$  and low pressure, 25%  $\text{Ca}(\text{CN})_2$ . The max. absorption of  $\text{HCN}$  by  $\text{CaO}$  is at  $300^\circ$ . It is concluded that prepn. of pure  $\text{Ca}(\text{CN})_2$  is difficult or impossible by methods now available since hydrolysis and the small soly. of  $\text{Ca}(\text{OH})_2$  results in much decompn. of  $\text{Ca}(\text{CN})_2$  when formed in aq. soln. A. R. M.



**Chlorides of bivalent molybdenum, tungsten and tantalum.** I. Koss, L. J. (Experimental work by Emma Haller, Herbert Helwig, Antonio Kohler and Robert Feit.) *Ber.* 55B, 1458-66(1922).—All 3 metals were found to form chloro-acids of analogous compn.,  $\text{HMoCl}_4 \cdot 4\text{H}_2\text{O}$ , contg. polynuclear complex anions of great stability. Results confirm Rosenheim and Kohn (*C. A.* 4, 1583) and correct formulas assigned by many other investigators. Methods of prepn. and analysis are detailed. Sublimation of purest metal powders gave only  $\text{MoCl}_3$  up to  $1200^\circ$  and  $\text{WCl}_5$ . With Mo the best yield was obtained by heating the powd. metal in H, then in N to remove H, then in a current of  $\text{COCl}_2$  at  $700-800^\circ$ . Temp. must be accurately controlled as at  $800^\circ$  chiefly  $\text{MoCl}_3$ , and below  $600^\circ$   $\text{MoCl}_5$  is formed. When sufficient dichloride is formed to protect the metal from further action of  $\text{COCl}_2$ , it is extd. with concd. HCl and the metal again heated successively with H, N and  $\text{COCl}_2$ .  $\text{HMoCl}_4 \cdot 4\text{H}_2\text{O}$  crystals, almost quant. from concd. HCl soln. Inferior but serviceable yields were obtained by heating to redness in an atm. of N a mixt. of 1 mol. pure dry  $\text{MoCl}_3$  and 1 mol. Al powder and an equal vol. of ignited quartz powder packed into a hard glass tube closed at one end. After completion of the clearly visible reaction, the product was extd. with concd. HCl, the liquid concd. and the chloro acid pptd. by extg. with HCl gas. The residue cannot be reworked.  $\text{COCl}_2$  was reduced by powd. W to C over a wide temp. range with formation of  $\text{WCl}_4$  and  $\text{WCl}_5$  but chiefly  $\text{WOCl}_2$ . Reduction of  $\text{WCl}_4$  by Na-Hg or the liquid Na-K-Hg was too violent to be usable. Reduction of  $\text{WCl}_4$  by Al proved best.  $\text{WCl}_4$  was prepd. by heating purest W powder with 0.1% Pt black as catalyzer in a current of Cl. The product, purified by repeated sublimation, was heated in N with Al and quartz, 3  $\text{WCl}_4$ :4 Al and an equal wt. of quartz powder being used. Subsequent treatment as in Mo gave  $\text{HW}_6\text{Cl}_4 \cdot 4\text{H}_2\text{O}$  in fine yellow needles. By a similar reduction of  $\text{TaCl}_5$  with Al, Zn or Pb powder  $\text{HTa}_6\text{Cl}_4 \cdot 4\text{H}_2\text{O}$  was obtained as a black-green cryst. powder. Pb is best on account of the small soly. of  $\text{PbCl}_2$ ; this is removed by  $\text{H}_2\text{S}$  without effect on the soln. Electro-reduction of fused  $\text{TaCl}_5$  formed some of the chloro-acid but was not efficient. The Mo and Ta acids are extremely stable; the W compd. gives off HCl in air. A. R. M.

**Reduction of tantalum pentachloride.** OTTO RUFF AND FRITZ THOMAS. *Ber.* 55B, 1466-73(1922).— $\text{TaCl}_5$  was heated with Al powder and  $\text{AlCl}_3$  in evacuated sealed tubes 2-3 hrs. at  $300^\circ$ . The dark green to black mixt. of chlorides thus formed when subsequently heated in air gives off  $\text{AlCl}_3$  and  $\text{TaCl}_5$  and the compn. of the residue depends on temp. of heating and on pressure. At 2-3 mm.  $\text{AlCl}_3$  distills off at about  $200^\circ$  and at  $250^\circ$  the residue has about the av. compn. of  $\text{TaCl}_4$ ; at  $350-400^\circ$  the residue approximates the compn. of  $\text{TaCl}_3$ ; at  $500^\circ$  it is between  $\text{TaCl}_3$  and  $\text{TaCl}_2$  and is then darker green than the original mixt. This residue is quite stable in air; when placed in water  $\text{TaCl}_3$  dissolves to an intense green soln.,  $\text{TaCl}_5$  is hydrolyzed and  $\text{TaCl}_2$  remains as a black-green residue. NaOH dissolves both  $\text{TaCl}_3$  and  $\text{TaCl}_2$  in the cold, at sufficient diln. without evolution of H and change of valence. The alk. solns. oxidize rapidly in air.  $\text{H}_2\text{O}_2$  forms brown pertantalate solns. which are decolorized on heating with evolution of O. The effect of various reagents upon the green aq. soln. of  $\text{TaCl}_3$  is detailed.

A. R. Minto

**Complex chlorides containing gold.** III. New cesium-auro chloride. H. L. WELLS. *Am. J. Sci.* 3, 414-6(1922); cf. *C. A.* 16, 1713, 2087.—From analysis and various other considerations the formula  $\text{Cs}_2\text{AuCl}_4$  is considered most probable. The new salt forms minute, deep-red crystals, quickly decompd. by water, usually with pptn. of the yellow double chloride,  $\text{CsAuCl}_2$ . It can be obtained from nearly neutral solns. highly concd. in  $\text{CsCl}$  but better from strongly acid solns. or even from concd. HCl soln. which increases the stability of the salt and removes the necessity of large excess of  $\text{CsCl}$ . It appears to be a unique type among the double halides inasmuch as its

very minute crystals, sparing soly. and increased stability in HCl, resembles the chlorostannates previously described.

A. R. M.

**Preparation and properties of organic chlorostannites and -stannates.** IV. Some chlorostannates. J. G. F. DRYCE. *Chem. News* 124, 310-13 (1922).—The following are described: *hydrazine chlorostannate*,  $(\text{NH}_2)_2\text{H}_2\text{SnCl}_4$ , thin, colorless plates which sep. on concg. and cooling a soln. of 2.3 g.  $\text{N}_2\text{H}_4 \cdot \text{HCl}$  in 50 cc. dil. HCl contg. 1.7 g.  $\text{SnCl}_4$ , m. p. above  $300^\circ$ . *Methylenediamine chlorostannate*,  $\text{CH}_2(\text{NH}_2)_2 \cdot \text{H}_2\text{SnCl}_4$ , small, rhombic prisms, sol. in water but hydrolyzed on standing or boiling by dissolving 8 g.  $\text{CH}_2\text{I}_2$  in 25 cc. concd. aq.  $\text{NH}_3$ , removing excess of  $\text{NH}_3$  on water bath at  $40-50^\circ$ , acidifying and warming with dil. HCl contg. 12 g.  $\text{SnCl}_4$ . *Ethylenediamine chlorostannate*,  $\text{C}_2\text{H}_4(\text{NH}_2)_2 \cdot \text{H}_2\text{SnCl}_4$ , pale brown plates, m. with decompn. at  $360^\circ$ , from 1.2 g.  $\text{C}_2\text{H}_4(\text{NH}_2)_2 \cdot \text{HCl}$  and 7 g.  $\text{SnCl}_4$  in 50 cc. dil. HCl. Similarly, from the constituent simple salts in dil. HCl soln., the *propylenediamine salt*,  $\text{C}_3\text{H}_6(\text{NH}_2)_2 \cdot \text{H}_2\text{SnCl}_4$ , and *benzidine salt*  $(\text{C}_6\text{H}_4\text{NH}_2)_2 \cdot \text{H}_2\text{SnCl}_4$ . Crystallographic data and drawings of crystals of propylene-, *p*-phenylene- and *m*-phenylenediamine salts are included.

A. R. M.

**Researches on the metallic carbonyls.** ROBT. L. MOND AND ALBERT E. WALLIS. *J. Chem. Soc.* 121, 29-32 (1922); (cf. Mond, Hirtz and Cowap, *C. A.* 4, 2118).—The compn. of Mo carbonyl, redetd. by 2 methods, corresponds to  $\text{Mo}_2(\text{CO})_8$ . It is insol. in the common solvents. Two years were required to prep. 170 mg. Ru gives 2 carbonyls, one volatile, cryst. and sol. in  $\text{C}_2\text{H}_6$ , and the other non-volatile, amorphous and insol. in  $\text{C}_2\text{H}_6$ , but sol. in  $\text{C}_2\text{H}_5\text{OH}$  and in  $\text{H}_2\text{O}$ . The formula of the latter appears to be  $\text{Ru}(\text{CO})_8$ . Optimum conditions are described for the prepn. of  $\text{Fe}(\text{CO})_5$ .  $\text{Ni}(\text{CO})_4$ , air and moist CO heated at  $200^\circ$  react to give a yellow deposit which is shown to be a colloidal basic Ni carbonate of varying compn.

T. E. DUNLAP

**Reduction of oxides by hydrogen.** E. BERGER. *Compt. rend.* 174, 1341-3 (1922); cf. *C. A.* 5, 3162 and *Compt. rend.* 158, 668).—From a study of the rates of reduction of  $\text{NiO}$  prepd. in various ways, it is concluded that there is no suboxide of Ni.

C. R. PARK

**Mechanism of the H-O reaction catalyzed by Pt (HOFMANN) 2.** Decomposition of  $\text{HNO}_2$  (KLEMMENC, POLLAK) 2.

CHAUDRON, GEORGES: *Etudes des réactions réversibles de l'hydrogène et de l'oxyde de carbone sur les oxydes métalliques*. Paris: Masson et Cie.

FAIRBANKS, J. N.: *Iron and its Compounds*. Vol. IX. Part 2 of "Textbook of Inorganic Chemistry." London: Charles Griffin & Co., Ltd. 265 pp. 18s. Reviewed in *Nature* 109, 505 (1922).

OSTWALD, WILHELM: *Grundlinien der anorganischen Chemie*. 5th Ed. revised Dresden and Leipzig: Th. Steinkopff. 861 pp. M 60.

WASSERMANN, FELIX and HOPFF, HEINRICH: *Grundriss der anorganischen Chemie*. 2nd Ed. revised. München: R. Müller & Steinecke. 180 pp. M 28.80.

## 7—ANALYTICAL CHEMISTRY

WILLIAM T. HALL

**The use of ultra-violet light in analysis.** A. F. KITCHING. *Analyst* 47, 206-7 (1922).—The fluorescent effects produced by ultra-violet light may be used to distinguish Japanese pearls from other localities, vegetable and mineral oils, wool and silk, casein used in sizing paper and other kinds of sizing and to detect water, acetone in alc., quinine, esculine, and the dye uranine.

W. T. H.

**Demonstration of the use of a universal indicator.** F. H. CANN. *J. Chem. Ed.* 196-7(1922).—J. Mohr in 1917 proposed the use of a mixt. of methyl red, methyl orange, phenolphthalein and phenolphthalein as indicator in water testing. Canning and Cannon have improved the indicator by adding bromothymol-blue or thymolphthalein and cresolphthalein or cresol red so that it shows changes in color corresponding to the spectrum and  $p_H$  values ranging from 3 to 11. C. showed in this demonstration that the colors produced are as follows:  $p_H$  3, pale red;  $p_H$  4, red;  $p_H$  5, orange-red;  $p_H$  6, orange;  $p_H$  6.5, yellow;  $p_H$  7, greenish yellow;  $p_H$  8, green;  $p_H$  9.5, blue;  $p_H$  10, violet;  $p_H$  11, reddish violet.

**The detection and determination of oxalic acid and its use as a standard in iodometry and argentometry.** L. ROSENTHALER. *Z. anal. Chem.* 51, 219-23(1922).—Oxalic acid is oxidized more readily by  $KIO_3$  than are other vegetable acids such as citric, malic and tartaric. By heating oxalic acid with  $KIO_3$  in dil. acid soln. a noticeable quantity of  $I_2$  is liberated in a few mins. with as little as 3 mg.  $H_2C_2O_4 \cdot 2H_2O$ . A study of the reaction shows that it takes place as follows:  $2IO_3^- + 5C_2O_4^{2-} + 12H^+ \rightarrow 6H_2O + 10CO_2 + I_2$ . If an excess of iodate is added, then, after the removal of the liberated  $I_2$ ,  $KI$  may be added and the  $I_2$  liberated by the reaction:  $IO_3^- + 5I^- + 6H^+ \rightarrow 3H_2O + 3I_2$  titrated with  $Na_2S_2O_4$ . Many have favored the use of a single standard to which all vol. solns. could be referred.  $Na_2C_2O_4$  as proposed by Sørensen is now used as a standard in iodometry and for  $KMnO_4$ . It may be used as a standard in iodometry as indicated above. Moreover, in neutral soln. an oxalate will ppt.  $Ag_2C_2O_4$  with  $Ag^+$  and the excess  $Ag^+$  is titrated with  $NH_4CNS$  soln. The  $Ag^+$  and  $CNS^-$  solns. can be standardized against  $Na_2C_2O_4$ .

**Symmetrical diphenylguanidine as a standard in acidimetry and alkalimetry.** C. A. CARLTON. *J. Am. Chem. Soc.* 44, 1469-74(1922).—Weigh about 1 g. of the standard into a 250 cc. beaker. Add 25 cc. alc. and 5 drops of 0.1% bromophenol blue in alc. Titrate with  $HCl$  until the soln., viewed against a yellow paper, appears colorless. As indicator 5 drops of bromophenol blue soln. and 2 of methyl red may be preferred. The published results all agree within 1 part in 1000 with themselves, with weighing  $AgCl$  and with the Gay-Lussac method using  $Na_2CO_3$ .

**Sodium sulfide as a substitute for hydrogen sulfide in qualitative analysis.** GIORGIO VORTMANN. *Boll. scient. tecnico* 3, No. 5; *Giorn. chim. ind. applicata* 3, 565(1921).—Prep. first a soln. in  $HCl$ , if possible; add an oxidizer ( $KClO_3$ ,  $HNO_3$ ,  $Br-H_2O$ ) to transform mercurous and stannous salts into mercuric and stannic, and to change  $Sb_2O_3$  and  $As_2O_3$  to  $Sb_2O_5$  and  $As_2O_5$ , resp. Add solid  $Na_2CO_3$  in slight excess, a few cc.  $NaOH$  and heat. If  $NH_3$  is set free, heat to boiling to drive it out, then ppt. with a 20% soln. of  $Na_2S$  in excess. The ppt. may contain  $Ag$ ,  $Cu$ ,  $Bi$ ,  $Cd$ ,  $Pb$ ,  $Fe$ ,  $Co$ ,  $Ni$ ,  $Mn$  and  $Zn$  as sulfides,  $U$  and  $Cr$  and rare earths as hydroxides,  $Ba$ ,  $Sr$ ,  $Ca$  and  $Mg$  as carbonates. Filtrate I may contain the sulfides of  $Hg$ ,  $Ni$ ,  $As$ ,  $Sb$ ,  $Su$  ( $Au$ ,  $Pt$ ),  $Mo$ ,  $W$ ,  $V$ . Treat ppt. I with dil.  $HCl$ ; in soln. II there may be present  $Fe$ ,  $Mn$ ,  $Zn$ ,  $U$ ,  $Cr$ ,  $Ba$ ,  $Sr$ ,  $Ca$ ,  $Mg(PO_4)$ ,  $Li$ , rare earths; ppt. II may contain  $Ag$ ,  $Cu$ ,  $Bi$ ,  $Cd$ ,  $Pb$ ,  $Co(Ni)$ . Heat soln. II and boil to drive out  $H_2S$ , then add  $Br-H_2O$  and  $Na_2CO_3$  in excess, filter. Filtrate III may contain  $Cr$ ,  $U(Mn)$ ; ppt. III— $Fe$ ,  $Mn$ ,  $Zn$ ,  $Ba$ ,  $Sr$ ,  $Ca$ ,  $Mg$ ,  $Li$ . Redissolve ppt. III in  $HCl$ ; ppt.  $Fe$  with  $AcONa$ , then  $Mn$  with  $NH_4OH$  and  $Br-H_2O$ ;  $Ba$ ,  $Sr$ ,  $Ca$  with  $(NH_4)_2CO_3$ ; the  $Zn$  in the filtrate with  $Na_2S$ . Treat the  $Mg$  and  $Li$ . Add  $NH_4Cl$  to filtrate I and boil:  $Hg$ ,  $Ni$ ,  $Al$  are pptd.; there remain in soln.  $Sb$ ,  $Sn$ ,  $As$ ,  $Mo$ ,  $W$  and  $V$  which can be sepd. and detected by known methods.  $Br-H_2O$  may be replaced by  $H_2O_2$ , or by  $Na_2O_2$  or even by  $K_2CO_3$ . Test for the above metals in another portion of the substance. The advantages of the  $Na_2S$  method are: (1) no special app. is required; (2)  $(NH_4)_2S$  is not needed; (3) the laboratory is less impure; (4) all the work may be done in one place; (5) the qual. analysis is simpler than with the use of  $H_2S$ , and it is least expensive.

ROBERT S. POSENER, JR.

**The precipitation of metals by hydrogen sulfide.** G. MCP. SMITH. *J. Am. Chem. Soc.* 44, 1800-2 (1922).—Owing to the extremely small quantities involved in the case of the concn. of the  $S^{--}$  ion in 0.3 *N* acid soln. and in the soly. products of some of the sulfides, the opinion is advanced that possibly  $HS^-$  rather than  $S^{--}$  is the active agent. It is also pointed out that according to the soly. product principle only 1  $H_2S^{--}$  ion can be present in each 1000 l. of satd. soln. In such cases the soly. product principle should not be interpreted too literally.

W. T. H.

**The use of conductivity titrations in precipitation analysis.** II. Conductivity titrations with silver nitrate. I. M. KOLTHOFF. *Z. anal. Chem.* 61, 229-40 (1922).—*Halides* may be titrated with accuracy in low concns. by Mohr's method but not if the soln. is highly colored. Cond. measurements are valuable in cases of the latter type: The numerous expts. described in this paper show that 2.5 milli-equivalents of halide in 25 cc. of soln. can be titrated accurately with the aid of cond. measurements and that in unsaturated soln. iodide can be titrated by  $Ag^+$  in the presence of  $Cl^-$  and not too much  $Br^-$ . By noting the turning point in the cond. curve it is possible to titrate *ferrocyanide* with  $Ag^+$  but the results are not as reliable as might be desired. It is interesting to note that the end point in a titration by the Mohr method takes place with the formation of  $Ag_3Fe(CN)_6$  but in cond. measurements with the formation of  $KAg_2Fe(CN)_6$ . Another turn in the cond. curve takes place with the formation of  $Ag_3Fe(CN)_6$ , however. *Ferricyanide* behaves normally and can be titrated exactly with the formation of  $Ag_3Fe(CN)_6$ . In titrating *cyanide* the cond. at first decreases owing to the formation of a complex ion,  $2CN^- + Ag^+ \rightarrow Ag(CN)_2^-$ . After 1 mol.  $Ag^+$  has been added for each 2 mols. of  $CN^-$  originally present, the cond. begins to increase for in the reaction  $Ag^+ + Ag(CN)_2^- \rightarrow 2AgCN$  an  $NO_3^-$  ion is added with each  $Ag^+$  and is more mobile than the complex which was present. When all of the  $CN^-$  is pptd., the cond. increases rapidly when more  $AgNO_3$  is added. When a mixt. of KCN and KCl is titrated a further loss in cond. takes place after the KCN is pptd. owing to the formation of  $AgCl$  but an expt. showed that cond. measurements could be used to det. both  $CN^-$  and  $Cl^-$  in the presence of one another. With *pyrophosphate* a deviation from the expected results was noticed and an error of about 1% is probably accounted for as in the ferrocyanide titration. *Chromate* can be titrated smoothly and the end-point corresponds to complete pptn. of  $Ag_2CrO_4$ . *Sulfite*, however, gave an end-point too soon and the ppt. was probably abnormal as in the case of ferrocyanide. As was to be expected, the cond. behavior of *thiosulfate* when titrated with  $Ag^+$  was erratic. *Oxalate*, *citrate*, *tartrate*, *succinate* and *salicylate* gave normal values.

W. T. H.

**The electrometric titration of uranium with potassium permanganate and potassium dichromate.** D. T. EWING AND E. F. ELDRIDGE. *J. Am. Chem. Soc.* 44, 1484-9 (1922).—If a soln. of uranyl sulfate is passed through a Jones' reductor, a part of the U is reduced to the tervalent state and the remainder is quadrivalent. If the reduced soln. is titrated electrometrically with  $KMnO_4$ , 2 end-points are obtained,—the first corresponds to the oxidation of tervalent U to quadrivalent U and varies with the rate at which the U soln. was passed through the reductor; the second corresponds exactly to the oxidation of quadrivalent to hexavalent U. Standard  $K_2Cr_2O_7$  may be used instead of  $KMnO_4$  but the U soln. should not contain more than 2 cc. of concd.  $H_2SO_4$  per 100 cc. The titration cell used in these expts. was fitted with a tight cover through which passed the bottom of the reductor tube, the bottom of the buret, a shaft for a stirrer, and tubes for the introduction and escape of  $CO_2$  gas, which was used to prevent atmospheric oxidation. The stirrer was fitted with a Hg seal. If Fe is present in the soln. there are three end-points; the first corresponds to the oxidation of U from 3 to 4, the second to the oxidation of U from 4 to 6 and the third to the oxidation of Fe from 2 to that of 3.

W. T. H.

A study of the sodium amalgam electrode for the determination of sodium ion. B. S. NEUBAUSEN. *J. Am. Chem. Soc.* 44, 1411-6(1922).—Prior to the investigation of the  $\text{Na}^+$  concn. in biol. fluids, it was deemed necessary to study the reliability of the Na-Hg electrode for detg. such concns. On the basis of the reading for 0.2 *N* NaCl, the voltage reading for 0.1 *N*  $\text{Na}^+$  checked closely but was too low for 0.02 *N* and 0.01 *N* solns. When  $\text{NH}_4^+$  was present it was impossible to make measurements if the soln. was more than 0.025 *N* with this salt. With 0.25 *N*  $\text{CaCl}_2$  there was a rapid generation of  $\text{H}_2$  and decompn. of the amalgam. With 0.25 *N*  $\text{ZnCl}_2$  there was no trouble. Added salt may affect the Na concn., may activate  $\text{Na}$  or the new cation may replace Na in the amalgam. The method therefore can be used only with caution.

Analytical methods of separating metal ions by means of compounds of the benzene series. I. Separation of aluminium from iron by means of *o*-phenetidine. K. CHALUPNY AND K. BREISCH. *Z. angew. Chem.* 35, 233-4(1922).—A soln. of *o*-phenetidine in alc. gives no ppt. with  $\text{Mn}^{++}$ ,  $\text{Zn}^{++}$ ,  $\text{Mg}^{++}$  and  $\text{Fe}^{++}$ . With  $\text{Co}^{++}$  and  $\text{Ni}^{++}$  a partial pptn. takes place. With  $\text{Fe}^{+++}$  a gradual pptn. of  $\text{Fe}(\text{OH})_3$  occurs in dil. solns. and in concd. solns. the phenetidine is oxidized to a violet compd. and eventually a black condensation product is pptd. With  $\text{Al}^{+++}$  a brown or yellowish ppt. is obtained of somewhat variable compn. Expts. showed that  $\text{Al}^{+++}$  can be sep'd. from  $\text{Fe}^{+++}$  by means of *o*-phenetidine; even though there is some oxidation in the filtrate no Fe ppt. is formed. Place the slightly acid soln. of  $\text{Fe}^{+++}$  and  $\text{Al}^{+++}$  in an Erlenmeyer flask and sat. with  $\text{H}_2\text{S}$  for about 10 mins. Drive out the excess  $\text{H}_2\text{S}$  by a stream of  $\text{CO}_2$ . Add  $(\text{NH}_4)_2\text{CO}_3$  until a slight permanent ppt. of  $\text{Al}(\text{OH})_3$  is obtained and dissolve this by the careful addition of HCl. To this soln. add a soln. of 5% *o*-phenetidine in alc. until at least 10 times as much org. compd. as Al is present; stopper the flask and heat to  $80^\circ$ . After a short time, filter through a filter cone, using filter paper pulp to prevent some of the ppt. running through. Ignite and weigh as  $\text{Al}_2\text{O}_3$ . To det. Al in an alloy contg. perhaps Cu, Ni, Mn and Zn, dissolve the sample in  $\text{HNO}_3$ , remove the Cu by electrolysis and ppt. the  $\text{Fe}^{+++}$  and  $\text{Al}^{+++}$  by the basic acetate method. Dissolve the ppt. in HCl and continue as outlined above. W. T. H.

Studies in gravimetric analysis. XX. The determination of manganese. L. W. WINKLER. *Z. angew. Chem.* 35, 234-5(1922); cf. *C. A.* 15, 3954.—The following procedure was tested. To the faintly acid soln. contg. 0.10-0.01 g. Mn in 100 cc., add 2 g. of  $\text{NH}_4\text{Cl}$  and heat to boiling in a 200-cc. beaker. Add slowly, while stirring, 10 cc. of 20%  $(\text{NH}_4)_2\text{HPO}_4$  soln. Allow to stand overnight, stirring occasionally during the first hour. Filter and wash first with 50 cc. of cold water which has been satd. with  $\text{MnNH}_4\text{PO}_4$  and finally with alc. Dry 2 hrs. at  $100^\circ$  and weigh as  $\text{Mn}_2(\text{NH}_4\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  or ignite to  $\text{Mn}_2\text{P}_2\text{O}_7$ . With quantities of Mn weighing about 0.4 g. the dried ppt. was found to weigh 1.2 mg. and the ignited ppt. 0.8 mg. too much; with 0.02 g. of Mn the weights of dried and ignited ppt. were within 0.2-0.3 mg. of the truth but with only 0.03 g. of Mn the dried ppt. was 1.9 mg. and the ignited ppt. 1.5 mg. too light.  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{NO}_3$  in fairly large amts. do no harm. KCl gives a slight positive error but with NaCl the positive error is serious, so that  $\text{Na}_2\text{HPO}_4$  cannot be used as precipitant. It is interesting to note that the similar ppts. produced with Cd and Mn each have 1 mol. of  $\text{H}_2\text{O}$ ,  $\text{ZnNH}_4\text{PO}_4$  has no water of crystal after drying at  $100^\circ$  and  $\text{MgNH}_4\text{PO}_4$  crystallizes with  $6\text{H}_2\text{O}$ .

Rapid determination of tungsten. FRANK G. ROHM. *Chem. Met. Eng.* 29, 107 (1922).—Dissolve 5 g. of borings in 90 cc. of 5 *N*  $\text{HNO}_3$ . When decomposition is complete add 20 cc. of *N*  $\text{KMnO}_4$  soln. and boil a few min. Clear the soln. by careful addition of  $\text{N}/3$   $\text{NaNO}_2$ , add a spoonful of paper pulp, 100 cc. of boiling water, 20 cc. of 10% HCl and 15 cc. of cinchonine hydrochloride soln. (75 g. cinchonine in 100 cc. of water).

Boil 5 min. and filter with suction. Wash with a soln. prepd. from 900 cc. water, 35 cc. of concd. HCl and 15 cc. of cinchonine reagent. Ignite and weigh as  $WO_3$ . The method is not applicable to steels which are very high in Cr or for most high-speed steels. W. T. H.

**The determination and separation of aluminum.** GERHART JANDER AND ERWIN WENDENFORS. *Z. angew. Chem.* 35, 244-5(1922).—Expts. showed that the usual methods of detg. Al are slightly inaccurate. Owing to its colloidal nature,  $Al(OH)_3$  soln. does not invariably remain to an appreciable extent when pptn. is effected by  $NH_4OH$ ,  $(NH_4)_2CO_3$ ,  $NH_4SCN$ ,  $Na_2S_2O_8$ ,  $KI-KIO_3$ , or  $(NH_4)_2HPO_4$ . This error is appreciable in the analysis of alloys rich in Al. When  $Al(NO_3)_3$  soln. is evapd. to dryness and the residue ignited, the resulting  $Al_2O_3$  corresponds to the wt. of Al in soln. To det. Al in the presence of small quantities of other metals, a method has been worked out which depends upon the volatilization of the Al as  $AlCl_3$  by heating the metal in a stream of dry  $HCl$  gas. Si originally present as silicide also distills and collects in the receiver as silicic acid. Small quantities of Mg and of Mn have also been found in the distillate. In the distn. residue, Cu, Fe, Si, Mn, Mg, etc. are to be found. In a soln. contg. Al and Mg, pptn. with  $NH_4OH$  serves to remove all but a little Al and the alumina sol in the filtrate does not interfere with the detn. of Mg as pyrophosphate. It is well, however, to add a little tartrate to make certain that no Al is in the ignited  $Mg_2P_2O_7$  ppt. In the expts. described, Al, Mg and Mn were detd. in alloys contg. from about 94 to 99% Al. The procedure is as follows: Place about 0.5 g. of metal shavings in a fairly large combustion boat. Insert the boat in a sleeve tube and the latter into a fairly short sublimation tube which is restricted at the front end and ends in a 10-bulb Meyer tube contg. a little cold water. The app. back of the Meyer bulb must be perfectly dry. Pass a current of dried HCl gas through the app. and heat the boat to about 300°. Make an air chamber around the sublimation tube by asbestos paper and suspend a thermometer in the chamber. Do not begin heating till the air is all expelled from the app. and raise the temp. slowly. When the reaction starts, heat is evolved so that the heat of the burner is unnecessary for a time. Finally heat for 20 min. at 200-300°. Cautiously introduce a little dil. HCl into the receiver, stopper and allow the violent reaction to take place between the dil. HCl and anhydrous  $AlCl_3$ . Finally add a little more acid and make sure that all the distillate is dissolved. Add 10 cc. of concd.  $HNO_3$  and evap. carefully to dryness. Repeat the treatment with  $HNO_3$  several times to make sure that all HCl is replaced. Dissolve in dil.  $HNO_3$  and filter off the  $SiO_2$ . Evap. the filtrate in a weighed Pt crucible and ignite to const. wt. In some cases the  $Al_2O_3$  contains a little  $Mn_2O_4$  and some  $MgO$ . Fuse it with  $KHSO_4$ , dissolve the melt in dil.  $H_2SO_4$  and ppt.  $Al^{+++}$  and  $Mn^{++}$  with  $NH_4OH$  and  $(NH_4)_2S$ . Det. the Mn in the ppt. by the usual colorimetric method and in the filtrate from the  $Al(OH)_3$  and  $MnS$ , ppt. the Mg as  $MgNH_4PO_4$  after adding a little tartaric acid. Correct the original wt. of  $Al_2O_3$  by deducting the  $Mn_2O_4$  and  $MgO$  found. W. T. H.

**New quantitative test for uranium.** H. D. BUELL. *J. Ind. Eng. Chem.* 14, 508 (1922).—When a soln. of uranyl salt in  $HNO_3$  is treated with Zn, a yellow deposit is obtained on the metal which is possibly  $UO_4 \cdot 2H_2O$ . The test is obtained if the soln. contains about 1 mg. of U per cc. W. T. H.

**The determination of small amounts of molybdenum in tungsten.** DOROTHY HALL. *J. Ind. Eng. Chem.* 14, 1462-5(1922).—Neutralize the acid soln. of molybdate and tungstate with 10%  $NaOH$ , add solid K xanthate, about 0.5 g. at a time, and several drops of 5%  $H_2SO_4$ . Add the acid drop by drop and agitate after each addition to prevent the formation of insol.  $H_2WO_4$ . Extract the red Mo compd. with  $CHCl_3$ , evap. to dryness and ppt. the Mo in the usual way as  $MoS_3$  and weigh as  $MoO_3$  or as  $PbMoO_4$ . In a soln. contg. as little as 0.01 mg. Mo can be detected by the red color of the xanthate.

Attempts to sep. Mo from Fe, Ni, V and U by the xanthate method were unsuccessful. These metals also form colored xanthates which are sol. in  $\text{CHCl}_3$ . W. T. H.

**The analytical chemistry of vanadium with reference to materials of iron smelting.** HERBERT BRIEFS. *Stahl u. Eisen* 42, 775-8(1922).—A new method for sepg. Cr and V is as follows: Acidify the soln. of vanadate and chromate with dil.  $\text{H}_2\text{SO}_4$  and add ZnO suspension to the boiling soln. Filter off the ppt. which contains all the V and some Cr, dissolve in  $\text{H}_2\text{SO}_4$  and repeat the treatment with ZnO. Filter and treat the combined filtrates, contg. all the Cr, with an excess of  $\text{Fe}^{++}$  in  $\text{H}_2\text{SO}_4$  soln. and titrate the excess with standard  $\text{KMnO}_4$ . Dissolve the Zn vanadate ppt. in dil.  $\text{H}_2\text{SO}_4$ , add 8 cc. concd.  $\text{H}_2\text{SO}_4$  and 0.2 g. oxalic acid and evap. to fumes, whereby vanadyl salt is obtained. Cool, and titrate with  $\text{KMnO}_4$  in the usual way. Methods for the sepn. of Fe from Cr and V were studied but none was found as satisfactory as that depending upon the removal of  $\text{FeCl}_3$  with ether. Fe and V may be pptd. together by ZnO or by  $\text{NH}_4\text{OH}$  and the ppt. fused with  $\text{Na}_2\text{CO}_3$ . The aq. ext. of the fused mass will contain all the V, which can then be pptd. by cupferron. In this way V can be sepd. from Fe and Cr. For the analysis of alloy steels the following method is recommended: Dissolve 3-5 g. of steel in  $\text{HNO}_3$ , evap. the resulting soln. to dryness and bake gently. Evap. again with concd.  $\text{HCl}$ , cool, dil. and filter off the  $\text{SiO}_2$  and  $\text{WO}_3$ . Conc. the filtrate to small vol. and carry out the Rothe ether sepn. Evap. off the ether from the aqueous soln., add concd.  $\text{H}_2\text{SO}_4$ , evap. to fumes, cool, dil., and ppt. Mn as  $\text{MnO}_2$  by boiling with  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ . Treat the filtrate as above with ZnO. Or, the  $\text{HCl}$  soln. obtained after treatment with ether may be oxidized with  $\text{KClO}_3$  and the V pptd. with cupferron. R. S. DEAN

**Determination of chromium in steel.** LUIGI LOSANO and ENRICO CAROZZI. *Giorn. chim. ind. applicata* 4, 197-200(1922).—Twelve of the well known methods for detg. Cr in materials rich in Fe were studied critically. The method depending upon the treatment of a soln. of  $\text{Cr}^{+++}$  and  $\text{Fe}^{+++}$  with alk.  $\text{Na}_2\text{O}_2$  and pptg. the sol.  $\text{CrO}_4^{--}$  with  $\text{Pb}^{++}$  in  $\text{AcOH}$  soln. was found satisfactory. Stead's method gave consistent results which were slightly low. The following method is recommended: Dissolve the alloy in 6 N  $\text{HNO}_3$ , or  $\text{H}_2\text{SO}_4$  dil., and oxidize with 20 cc. of 6%  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  soln. in the presence of Ag as catalyzer. Boil until the liquid is a clear yellow in color, adding a little filter paper to help decompose  $\text{MnO}_4^-$ . Cool, add 25 cc. of concd.  $\text{HNO}_3$ , a measured vol. of arsenite soln. and titrate the excess with  $\text{KMnO}_4$ . The results obtained colorimetrically were unsatisfactory. ROBERT S. POSMONTIER

**Some modern methods for the detection of arsenic.** A. J. JONES. *Pharm. J.* 108, 193-4(1922).—The various methods of destroying org. matter are given. For tangible amts. of As to be detd., ppt. in  $\text{HCl}$  soln. by adding  $\text{ZnS}$ ; or use the method of Evans (*C. A.* 14, 1093). For minute amts., use Marsh's test, but this is not reliable in presence of any Hg, or of much Cu or Fe. For accurate work, resort to previous distn. of the As material with  $\text{HCl}$ ,  $\text{FeS}$  and  $\text{KBr}$ , collect in  $\text{HNO}_3$  conc. again with  $\text{H}_2\text{SO}_4$ , reduce with  $\text{NaHSO}_3$ , boil off the  $\text{SO}_2$ , then use an aliquot part in the Marsh test. Run a blank with the accessory materials. S. WALDBOTT

**A "micro-Kjeldahl" method of determining nitrogen.** A. R. LING and Wm. J. PRACE. *J. Soc. Chem. Ind.* 41, 149-51T(1921).—Weigh out substance equiv. to 1-0.1 mg. of N together with 1 g.  $\text{K}_2\text{SO}_4$  and 0.02 g.  $\text{CuSO}_4$  into a hard-glass boiling tube. Add 8 cc. concd.  $\text{H}_2\text{SO}_4$  and 2 drops  $\text{H}_2\text{PtCl}_6$  soln. Place a small funnel in the neck of the tube and boil until the liquid is colorless. Cool, add 15 cc. of water and boil to expel  $\text{SO}_2$ . Cool and introduce the soln. into a 300-cc. distg. flask, make alk. with 40%  $\text{NaOH}$  and distil through a condenser into 50 cc. of water contained in a 250-cc. flask, using some freshly ignited, porous porcelain in the distg. flask to prevent bumping. To the distillate add 1.5 cc. of 40%  $\text{NaOH}$  soln., 5 cc. of Nessler reagent and dil. to

250 cc. Prep. a stock soln. contg. 1 mg. N per cc. by dissolving 4.716 g. of  $(\text{NH}_4)_2\text{SO}_4$  and 200 cc. of  $\text{N H}_2\text{SO}_4$  in water to make 1 l. Take 1 cc. of this soln., add 150 cc. of water and Nessler reagent exactly as in the analysis. Compare the colors of 10-cc. portions of each soln. by looking down upon the surfaces in Nessler tubes. From the stronger soln. withdraw portions with a pipet graduated to 0.01 cc. until the colors match, making a final comparison with equal vols. of liquids. Solns. with lower concn. than the standard gave more color than if the color was directly proportional to the concn. of  $\text{NH}_3$ , so that it is necessary to apply an empirical correction to get the true % N. The correction is found by testing with Nessler soln. in the above manner, solns. of known concn. being used.

W. T. H.

**Rapid determination of sulfur.** LUIGI LOSANA. *Giorn. chim. ind. applicata* **4**, 204-6(1922).—Heat a quantity of material corresponding to not more than 0.05 g. S in an ignition tube with a mixt. of Fe powder and  $\text{NaHCO}_3$ , covering with a layer of Fe powder. Place the ignited mass in an evolution flask, treat with acid and absorb the  $\text{H}_2\text{S}$  in  $(\text{AcO})_2\text{Zn}$  soln. Det. the S content iodometrically as in the detn. of S in Fe and steel. It is recommended to use a current of  $\text{CO}_2$  to expel air at the start and to sweep out all  $\text{H}_2\text{S}$  at the end. Org. substances do not always respond to this treatment. They should be heated first with  $\text{CuO}$  or  $\text{PbCrO}_4$  and the product treated as above after mixing intimately with flux in a mortar.

ROBERT S. POSMONTIER

**Determination of arsenic acid.** L. ROSENTHALER. *Z. anal. Chem.* **61**, 222-9 (1922).—About 15 yrs. ago R. published a method for the detn. of  $\text{AsO}_4^{---}$  based on the reaction:  $\text{AsO}_4^{---} + 2\text{I}^- + 2\text{H}^+ \longrightarrow \text{AsO}_3^{---} + \text{I}_2 + \text{H}_2\text{O}$ . Recently Fleury (*C. A.* **14**, 2600) has criticized the method. The results of some 22 expts. apparently prove that the objections raised by Fleury are not valid.

W. T. H.

**Colorimetric determination of phosphorus.** LUIGI LOSANA. *Giorn. chim. ind. applicata* **4**, 60-2(1922).—The blue reduction product formed when a ppt. of  $(\text{NH}_4)_2\text{PO}_4 \cdot 12\text{MoO}_3$  is treated with hot  $\text{Na}_2\text{S}_2\text{O}_3$  soln. is the basis of this method. Transfer the asbestos felt contg. the washed ppt. to a small beaker, add 20 cc. of 15%  $\text{Na}_2\text{S}_2\text{O}_3$  soln. and heat 10 min. at  $80^\circ$ . Filter into a 100-cc. calibrated flask and wash with hot water. Compare the color of 10 cc. of the soln. with that obtained similarly with 0.0618 g. of pure yellow ppt. L. has devised 2 novel forms of *colorimeter* to be used in this analysis. In one form a mirror image of the soln. is compared directly with the color of a piece of blue glass and the soln. is run out until the colors match. In the other form the standard and analyzed soln. are viewed together. The tubes contg. the soln. and that of the standard are graduated so that the final vols. can be read directly.

ROBERT S. POSMONTIER

**Determination of free chlorine and hypochlorous acid in concentrated salt solutions.** M. C. TAYLOR AND C. A. GAMMAL. *J. Ind. Eng. Chem.* **14**, 632-5(1922).—When  $\text{Cl}_2$  is removed by aeration of a soln. of brine, some  $\text{Cl}_2$  is likely to be formed from the  $\text{HClO}$  originally present. In this paper it is shown that the rate of removal of  $\text{Cl}_2$  during aeration is approx. a linear function of the free  $\text{Cl}_2$  content as long as any of the original gas remains in soln. When all the original  $\text{Cl}_2$  is removed, the rate of removal varies with the square of the  $\text{HClO}$  present. The graph representing the rate of  $\text{Cl}_2$  removal will consist of 2 radically different sections so that it is possible to est. the quantity of  $\text{Cl}_2$  originally present. The analysis consists of 3 steps: first, the available  $\text{Cl}_2$  (free  $\text{Cl}_2$  and  $\text{Cl}$  present as  $\text{HClO}$  or  $\text{NaClO}$ ) is detd. by adding a known vol. of acid, some  $\text{KI}$  and titrating the liberated  $\text{I}_2$  with  $\text{Na}_2\text{S}_2\text{O}_3$ ; second, the excess acid remaining after the first titration is detd. by titrating the  $\text{I}_2$  liberated by treatment with a mixt. of  $\text{KI}$  and  $\text{KIO}_3$ ; third, the rate at which free  $\text{Cl}_2$  is driven off by aeration is detd.

W. T. H.

**Effect of adsorption by stannic sulfide upon the analysis of phosphates.** SUETARO



**KIKUCHI.** *J. Chem. Soc. (Japan)* **43**, 329-33(1922).—Lord showed that if  $\text{PO}_4$  is estd. after Sn is removed as sulfide (C. A. 13, 1804), there is a considerable loss, which, according to K., is due to adsorption by  $\text{SnS}_2$ . Interference of Sn under difficult conditions was investigated. Solns. of  $\text{Na}_2\text{HPO}_4$  (0.0083 g.  $\text{P}_2\text{O}_5$  per l.) and  $\text{Na}_2\text{SnCl}_6$  (0.0086 g. Sn per l.) were used. Definite amts. of these solns. were made to 100 cc.,  $\text{H}_2\text{S}$  was passed and the filtrate analyzed for  $\text{PO}_4$  by Mg mixt. The results show that the loss of  $\text{PO}_4$  is due to adsorption by  $\text{SnS}_2$ , its extent being proportional to the concn. of Sn, not to that of  $\text{PO}_4$ .  $\text{SnS}$  does not adsorb and, therefore, does not interfere with the estn. of  $\text{PO}_4$ . If Sn is previously reduced by Zn under  $\text{CO}_2$ , and  $\text{HCl}$  is added to dissolve metallic Sn, which is then removed as  $\text{SnS}$ ,  $\text{PO}_4$  can be estd. accurately by the ordinary method. S. T.

**Exact determination of the sulfate radical in sodium sulfate.** **MOROTARO MATSU** AND **SEN-ICHI KIMURA.** *J. Chem. Ind. (Japan)* **24**, 1039-53(1921).—A comparison was made of (A) the slow method and (B) the rapid method of Allen and Johnston (C. A. 4, 1955), (C) the method of Johnston and Adams (C. A. 5, 2456), (D) that of Allen and Bishop (C. A. 6, 3245) and (E) that of Hinz and Weber (Z. anal. Chem. 31, (1906)). All gave satisfactory results if corrections were made for  $\text{BaSO}_4$  in the supernatant liquid, according to Treadway-Hall (Vol. 2, 466), for  $\text{BaCl}_2$  occluded in the ppt., according to Hullet and Duschak (Z. anorg. Chem. 1904), and for  $\text{Na}_2\text{SO}_4$  occluded in the ppt., according to Allen and Johnston (C. A. 4, 1955). It is concluded that A gives min. errors with these corrections and C without them. S. T.

**A volumetric method for the evaluation of hyposulfurous and sulfoxypic acids.** **FERRUCCIO DE BACHO.** *Z. anal. Chem.* **61**, 209-19(1922).—Many methods have been proposed for the analysis of solns. contg.  $\text{H}_2\text{S}_2\text{O}_4$  or  $\text{H}_2\text{SO}_3$  but accurate results are obtained only when the reaction takes place out of contact with air, which causes oxidation. The new method can be carried out while the soln. is in contact with air. In the presence of an excess of  $\text{HCHO}$ , the following reactions take place when a neutral soln. is titrated with  $\text{I}_2$ : (a)  $\text{S}_2\text{O}_4^{--} + 3\text{H}_2\text{O} + 2\text{I}_2 \rightarrow \text{HSO}_3^- + \text{SO}_4^{--} + 5\text{H}^+ + 4\text{I}^-$ ; (b)  $\text{HSO}_3^- + 2\text{H}_2\text{O} + 2\text{I}_2 \rightarrow \text{SO}_4^{--} + 5\text{H}^+ + 4\text{I}^-$ . The  $\text{HSO}_3^-$  formed in equation (a) forms a complex with  $\text{HCHO}$  and does not react with  $\text{I}_2$  or with  $\text{NaOH}$  in the analysis. Thiosulfuric acid and its salts are the only related S acids which interfere with the  $\text{I}_2$  titration but with  $\text{Na}_2\text{S}_2\text{O}_3$  no acid is liberated:  $2\text{S}_2\text{O}_3^{--} + \text{I}_2 \rightarrow \text{S}_4\text{O}_6^{--} + 2\text{I}^-$ . If, therefore, the soln. is titrated with  $\text{I}_2$  and then with  $\text{NaOH}$  of the same normal concn., the vol. of  $\text{NaOH}$  used multiplied by 4/5 will give the vol. of  $\text{I}_2$  which reacted with  $\text{Na}_2\text{S}_2\text{O}_4$  or  $\text{NaHSO}_3$  and this subtracted from the total vol. of  $\text{I}_2$  will give the  $\text{Na}_2\text{S}_2\text{O}_4$  equivalent. The method is as follows: Weigh out in a glass-stoppered weighing beaker material equivalent to about 1 g. of  $\text{Na}_2\text{S}_2\text{O}_4$  and add 10 cc. of pure, concd.  $\text{HCHO}$ . Crush the crystals in the liquid until they dissolve, add 5 cc. of water, rinse down the sides of the beaker with a little water, stopper and allow to stand for about 20 mins. Transfer to a 500-cc. measuring flask, add 150-200 cc. of water and 2 drops of 0.1% methyl orange. Add  $N$   $\text{H}_2\text{SO}_4$  to acid reaction but carefully avoid an excess. Make up to 500 cc., mix and use 50 cc. for the titrations. To the aliquot part add phenolphthalein and  $\text{CO}_2$ -free  $\text{NaOH}$  or  $\text{Ba(OH)}_2$  until a faint pink coloration is obtained and then titrate with 0.1  $N$   $\text{I}_2$  soln. using starch paste as indicator. Then decolorize the soln. by a drop of 0.1  $N$   $\text{Na}_2\text{S}_2\text{O}_3$  soln. and titrate with  $\text{NaOH}$ . All water used in the analysis should be freed from  $\text{CO}_2$  by boiling. W. T. H.

**The analysis of liquid nitrogen peroxide.** **A. SANFOURCHE.** *Bull. soc. chim.* **31**, 316-9(1922).—Commercial  $\text{NO}_2$  contains besides its polymer  $\text{N}_2\text{O}_4$  some  $\text{N}_2\text{O}_3$  and some  $\text{HNO}_3$ . A little  $\text{N}_2\text{O}_3$  is sometimes advantageous as pure  $\text{N}_2\text{O}_4$  freezes at  $-9^\circ$  whereas the  $\text{N}_2\text{O}_3$ - $\text{N}_2\text{O}_4$  eutectic freezes at  $-112^\circ$ . Special precautions are required in taking a representative sample for analysis. The  $\text{HNO}_3$  is easily detd. by allowing the liquid

to evap., dilg. the residue and titrating with *N* NaOH soln. To det.  $\text{N}_2\text{O}_4$  and  $\text{N}_2\text{O}_5$  dissolve the cold liquid in cold  $\text{H}_2\text{SO}_4$ , and use aliquot parts for the further analysis. The presence of the  $\text{H}_2\text{SO}_4$ , and the formation of nitrosylsulfuric acid or nitrosulfonic acid, prevent loss of the desired constituents without changing the behavior on the nitrometer or in the  $\text{KMnO}_4$  titration. By means of the nitrometer det. the  $\text{NO}$  produced from  $\text{N}_2\text{O}_4$ ,  $\text{N}_2\text{O}_5$  and  $\text{HNO}_3$  and by titration with  $\text{KMnO}_4$  det. the  $\text{HNO}_3$  originally present and that formed from the reaction  $2 \text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HNO}_3 + \text{HNO}_2$ . This gives all the data necessary.

W. T. H.

**Checking assay samples by screening analysis.** A. W. ALLEN. *Eng. Mining J.-Press* 113, 823-4(1922).—In the wet-chemical bulk treatment of ores, the extn. is usually based on the difference between the amt. of metal in the charge and in the residue samples. In order that the theoretical estimate shall tally closely with actual recovery, the screening analyses of both head samples and residue should be in close agreement, for the metal is seldom distributed evenly among the various sizings. It sometimes happens on drying a residue sample of crushed ore after wet-metallurgical treatment that a cohesion of the finer particles occurs which affects the screening analysis. In such cases it is desirable to wet the head sample retained for screen analysis, and afterward subject it to a drying and screening treatment identical with that given to the residue sample. It is seldom practicable in routine work to make screening analyses by methods that insure absolute accuracy. The essential precaution is to see that the physical characteristics of the material and the conditions of the test are maintained constant in every respect.

S. G. SIMPSON

**The use of potassium bromate in volumetric organic analysis.** T. CALLAN AND J. A. R. HENDERSON. *J. Soc. Chem. Ind.* 41, 161-4T(1922).—Bromination takes place more readily with an acid soln. of  $\text{KBrO}_3$  and  $\text{KBr}$  than with free  $\text{Br}_2$ . The reaction takes place so smoothly that in many cases a titration can be made by the  $\text{KBrO}_3$  soln. and the end-point detd. by the liberation of  $\text{I}_2$  on iodo-starch paper moistened with the soln. This method of analysis was applied to aniline by Vaubel and to toluidines by Reinhardt and by Winther. In this paper results are given which were obtained in the analysis of *dimethylaniline*, *sulfanilic acid*, *diphenylamine*, *thiocarbanilide* and *mixts. of dinitrophenol and picric acid*. With dimethylaniline one atom of  $\text{Br}$  per mol. is absorbed if the temp. is at  $0-5^\circ$ , 2 atoms of  $\text{Br}$  at  $40-60^\circ$  and 3 atoms of  $\text{Br}$  at  $60-70^\circ$ . With sulfanilic acid, 3 atoms of  $\text{Br}$  are absorbed at  $60-70^\circ$  but at lower temps. it is possible to get a transient end-point with only 2 atoms of  $\text{Br}$  absorbed. With diphenylamine, 3 atoms of  $\text{Br}$  are absorbed at  $60-70^\circ$ . Two atoms of  $\text{Br}$  are absorbed by *p*-nitrophenol but with 1,2,4-dinitrophenol only 1 atom of  $\text{Br}$  is absorbed. Picric acid does not absorb any  $\text{Br}$ . Thiocarbanilide titrates smoothly in glacial  $\text{AcOH}$  soln. and one mol. absorbs 4 atoms of  $\text{Br}$ . This appears to be the only rapid volumetric method which has been proposed for the analysis of thiocarbanilide.

W. T. H.

**Analysis of acetic anhydride.** A. RECLAIRE. *Perfumery Essent. Oil Rec.* 13, 148-9(1922).—Weigh out 10 g. of sample into a 250-cc. flask, add 75 cc. of  $\text{CO}_2$ -free distd.  $\text{H}_2\text{O}$ , heat 15 min. on a steam bath in connection with a reflux, then after cooling, and rinsing off condenser and cork, make up to 500 cc. with  $\text{CO}_2$ -free  $\text{H}_2\text{O}$ , and titrate 50 cc. of the soln. with 0.5 *N*  $\text{KOH}$  (carbonate-free) in the presence of phenolphthalein.

W. O. E.

MACMAHON, PERCY ALEXANDER: *An Introduction to Combinatory Analysis*. New York: Macmillan & Co. 71 pp. \$2.60.

PULSFER, H. B.: *The Determination of Sulfur in Iron and Steel*. Easton, Pa.: Chemical Publishing Co. \$2.50. Reviewed in *Eng. Mining J.* 113, 970(1922).

SMYTH, G. MCP.: *A Course of Instruction in Quantitative Chemical Analysis for*

**Beginning Students: With Explanatory Notes, Questions, and Analytical Problems.**  
 Revised ed. New York: Macmillan Co. London: Macmillan & Co., Ltd. 218 pp.  
 12s. Reviewed in *Nature* 109, 709(1922).

## 8—MINERALOGICAL AND GEOLOGICAL CHEMISTRY

EDGAR T. WHERRY AND WALTER F. HUNT

**A contribution to the theory of solid solutions, mix-crystal formation and isomorphism.** J. JAKOB. *Z. Krist.* 56, 295-304(1921); cf. *C. A.* 15, 36, 3260.—On the basis of highly complex coordinate formulas of some of the silicate minerals which show solid soln. relations, it is concluded that solid soln. is contingent on (1) similar spacial arrangement of mols. and (2) pure soln. phenomena. The at. d. in the vicinity of a coordinate nucleus must be similar, the more distant atoms or groups being capable of considerable variation without showing much effect. For at. groups taken up in non-stoichiometric proportions the term "chemico-constitutionally dissolved" is proposed. Case (2) is illustrated by albite and anorthite, which appear to be stoichiometrically dissimilar, selective chem. affinity forces here playing a role in detg. which compds. will and which will not form solid solns. E. T. W.

**The statement of theoretical compositions of minerals.** E. T. WHERRY. *Am. Mineral.* 7, 32-3(1922).—Examples are given to uphold the view that only when the at. wts. of all the elements concerned in a mineral become known with greater finality than many of them are at present, will extension of the theoretical compns. beyond one decimal be justified. E. T. W.

**Some problems of mineral genesis in South Africa.** CHARLES PALACHE. *Am. Mineral.* 7, 37-45(1922).—A review of problems, in part geo-chem., which need study. E. T. W.

**Crystallography of three minerals from Rhode Island.** A. C. HAWKINS. *Am. Mineral.* 7, 27-9(1922).—Data are given for hematite, epidote and apatite, several new forms being present. E. T. W.

**Eakleite from Isle Royale, Michigan.** W. F. FOSHAG AND E. S. LARSEN. *Am. Mineral.* 7, 23-4(1922).—A fibrous mineral labeled wollastonite proved to have the optical properties of the new mineral eakleite (*C. A.* 11, 2082) and analysis gave:  $\text{SiO}_2$  50.88,  $\text{Fe}_2\text{O}_3$  1.32,  $\text{CaO}$  42.88,  $\text{MgO}$  1.10,  $\text{Na}_2\text{O}$  0.55,  $\text{H}_2\text{O}$  -0.12,  $\text{H}_2\text{O} + 3.68$ , sum 100.53%. This is sufficiently close to the original analysis and the theory to establish it as a new occurrence of eakleite. E. T. W.

**Ore deposits and their genesis in relation to geographical distribution.** J. W. GREGORY. *J. Chem. Soc.* 121, 750-72(1922).—Local occurrence of ores is to be explained by periodic elevation of the barysphere (interior core of metal) having raised rocks rich in metal near to the surface. The domes of the barysphere would be local areas of high temp., surrounded by fractures which would allow lode forming solns. to enter the lithosphere (rock crust). The nature of the primary ores in such zones would depend on the depth and nature of the fractures. EDW. F. HOLDEN

**Iron ores of the Adirondack region.** F. L. NASON. *Iron Age* 109, 1592(1922).—Prospective tonnage of "gray gneiss" and titaniferous Fe ores is 1,736 million tons. The magnetic concentrates are high grade, up to 68% Fe, and the estd. yield from the 1,500 million tons of non-titaniferous ores is 625 million tons. EDW. F. HOLDEN

**A rich nickel ore.** A. F. CROSS. *J. Chem. Met. Mining Soc. S. Africa* 21, 126 (1921).—A rich Ni ore found near the talc mines on the farm "Bon Accord" north of the branch line to Barberton, Transvaal, showed on anal.:  $\text{NiO}$  40.30,  $\text{FeO}$  49.30,  $\text{P}_2\text{O}_5$  0.13,  $\text{CaO}$  0.20,  $\text{SiO}_2$  6.50, loss on ign. 2.15, sum 98.55%; sp. gr. 4.6. It has been named *treporite*. S. C. GORDON

**Platinum in the quartz veins of southwest Oregon.** A. E. KELLOGG. *Eng. Mining J.-Press* 113, 1000(1922).—Blue vein quartz in the Highland mine, Gold Hill district, contained a high % Pt, while quartz from Curry Co. ran 10-20 oz. Pt per ton.

EDW. F. HOLDEN

**Sulfur resources of Chile.** H. G. OFFICER. *Eng. Mining J.-Press* 113, 995-1000(1922).—S deposits occur at several places in the Andes along cracks in the flanks of volcanoes. The beds reach 20-30 ft. in thickness, and 50-95% S, this being recovered by distn. An incomplete estimate of the reserves of S is 3,418,000 tons. E. F. H.

**Mica.** OLIVER BOWLES. *Bur. of Mines, Repts. of Invest. No. 2357*, 46 pp.(1922).—This paper discusses: the properties, origin and occurrence of mica; its imperfections; statistics of production and consumption by countries and states of the U. S.; uses, grades, and specifications; mining methods; trimming and cutting methods; ground mica manufacture; distribution of deposits; and recent developments in foreign countries.

EDW. F. HOLDEN

**What is the reason that the earth contains a preponderant amount of iron?** W. WESTPHAL. *Naturwissenschaften* 10, 260(1922).—Based on the Kant-LaPlace theory, the sun must once have contained a relatively large amt. of Fe which before the formation of the earth must have been as preponderant as the present Ca content.

C. C. DAVIS

**Bauxite and lignites as indicators in determining the climate of the Tertiary period in Dalmatia.** FRITZ KERNER-MARILAU. *Sitzb. Akad. Wiss., Wien, Abt. I* 130, 35-70(1922).—A study of the plants has resulted in ests. of temp. and rainfall of each of the 4 subdivisions of the Tertiary period.

C. C. DAVIS

**Soda lakes.** CARL ELSCHNER. *Chem.-Ztg.* 46, 450(1922).—The saline water at Owen's Lake, Cal. is treated as follows: (1) Insol. matter and Ca and Mg carbonates are pptd. in pools, (2) trona is crystd. out in other pools by the sun's heat, (3) the liquid is drawn off before salt deposits. In cold weather it is largely the normal carbonate that separates out; leading CO<sub>2</sub> into the pools aids the formation of the desired bicarbonate.

EDW. F. HOLDEN

An apparatus for handling deliquescent crystals (SLAWSON) 1.

BRAUNS, R.: *Anleitung zum Bestimmen der Mineralien* (Fuchs). 7th Ed. Gies-sen: Alfred Toepelmann. 223 pp. Reviewed in *Am. Mineral.* 7, 30(1922).

GROTH, P. and MIELEITNER, K.: *Mineralogische Tabellen*. Munich: R. Olden-bourg. 176 pp. Reviewed in *Am. Mineral.* 7, 30-1(1922).

BEHAGHEL, GEORG: *Die Eisen- und Manganerze Osteuropas*. Leipzig and Berlin: B. G. Teubner. 361 pp.

KLOCKMANN, FRIEDRICH: *Lehrbuch der Mineralogie*. 7th and 8th revised Ed. Stuttgart: F. Enke. 667 pp.

## 9—METALLURGY AND METALLOGRAPHY

D. J. DEMOREST, ROBERT S. WILLIAMS.

**The sulfur dioxide leaching process.** C. E. VAN BARNEVELD AND E. S. LEAVER. *Bur. Mines Repts. Investigations* No. 2350, 15 pp.(1922).—The process was devised to provide a cheap and efficient method for treating the porphyry Cu ores of the Southwest. The ores contain a mixt. of sulfide and oxide Cu. Flotation recovers only the sulfide. Acid-leaching recovers only oxide, while roasting of the ore is not commercially possible. The new SO<sub>2</sub> leaching process converts oxide Cu to sol. CuSO<sub>4</sub> in a continuous process by means of hot SO<sub>2</sub>. The ore ranging in fineness from 20 to 48 mesh, and pulped with water contg. the usual proportion of reclaimed mill liquor, is treated counter-current

with dil.  $\text{SO}_2$  roaster gas contg. a large excess of  $\text{O}_2$ . The dissolved Cu may be pptd. as cement Cu in the pulp, and then recovered therefrom by flotation, which would also recover most of the sulfide Cu. About  $\frac{1}{2}$  of the sulfide Cu is oxidized and dissolved while the extn. of the oxide Cu is 96-98%. Large-scale expts. are being carried on at the Southwest Expt. Station, while earlier tests were made at Tucson, Miami, and Clifton, Ariz. These tests are described: The leaching is done in a revolving wooden drum which splashes and distributes the pulp in such a way as to afford perfect contact with the reagent, avoiding all percolation difficulties. The roaster gases contg. 5%  $\text{SO}_2$  enter the drum at  $175^\circ$  and leave it cold, so that all Cu sulfite is converted to sulfate, the absorption of  $\text{SO}_2$  below  $50^\circ$  being negligible. It is necessary, however, to aerate the discharge from the drum in order to complete this conversion and  $\text{SO}_2$  removal. The temp. must be carefully controlled, but this affords no difficulty; there are no fine adjustments in the process, the reagent is cheap, the plant is compact and inexpensive, power requirements are small, and operation is easy. The Cu may be recovered from soln. by any of the usual methods, but the recovery as cement Cu by flotation, while not yet perfected, appears most promising. To be successful the Cu must be pptd. on iron sponge instead of scrap or pig iron. The sponge may be made by reduction of the pyrite used to generate the  $\text{SO}_2$ , and its effect is to produce the cement Cu in larger particles easily floated.

A. BUTTS

**Ajo enterprise of the New Cornelia Copper Co.** A. W. ALLEN. *Eng. Mining J.-Press* 113, 952-6, 1003-8, 1051-3(1922).—An account of the history of development, geology, sampling, development of the leaching process, equipment and operation.

A. BUTTS

**Heat requirements in chloridizing volatilization.** RUDOLF GAHL. *Eng. Mining J.-Press* 113, 957-8(1922).—Fuel consumption appears to be the crucial point as regards the com. success of chloridizing volatilization. Modification of furnace to reduce fuel requirement must be worked on. The amt. of fuel depends chiefly on three factors—tonnage, draft, and radiation; a formula is developed by which the fuel may be calcd. from these factors.

A. BUTTS

**Preparation of iron directly (from raw coal).** H. ILIES. *Feuerungstechnik* 10, 161-4(1922).—A review.

ERNEST W. THIELER

**Buckets and skips for blast furnaces.** D. E. ROBERTS. *Iron Age* 109, 1595-8 (1922).—This is a discussion of the faults and advantages of this system over the other systems in use at different furnaces in this or other countries. Some of the principal faults are rigidity, sepn. of fines and coarse and less chance for fluctuations of charge.

W. A. MUELLER

**Gas and air valves for open-hearth furnaces.** WM. C. BULMER. *Blast Furnace and Steel Plant* 10, 302-6(1922).—The history of the air and gas valve construction of former days is cited together with the more modern types. The chief essential of a valve for this purpose is free passage. In some instances the draft loss resulting from poor valves amounted to as much as 60% of the total draft and in one case where trouble was encountered with this phase the valves required more draft than was produced to produce flow through them. Ordinarily 1 sq. ft. area should be present per 10 t. capacity of furnace. Water-cooled valves should be water-tight and in all cases warping should be guarded against.

W. A. MUELLER

**Metal spraying process.** N. MEURER. *Elektrochem. Z.* 28, 5-6, 13-6(1921).—A detailed review.

H. G.

**New uses for zirconium (KIRCHNER) 18. Curves of cooling and heating (ARIANO) 2.**

CONDOUCHÉ, AUGUSTE: *Les progrès de la métallurgie du cuivre*. Paris: Masson et Cie. 254 pp. Fr. 14.

**Glesserei-Handbuch.** Edited by Verein Deutscher Eisenglessereien Glesserei-  
verband in Düsseldorf. München: R. Oldenbourg. 264 pp. M 300. Reviewed  
in *Mech. Eng.* 44, 342(1922).

**JULIAN, H. FORBES, and SMART, EDGAR:** Cyaniding Gold and Silver Ores. 3rd  
Ed. revized and enlarged by A. W. Allen. London: Griffin. 441 pp. 38s.

**KRAUSE, HUGO:** Metallfärbung. Die wichtigsten Verfahren zur Oberflächen-  
färbung von Metallgegenständen. Berlin: Julius Springer. 205 pp. M 56.

**LIPPMANN, OTTO:** Härtetechnik, Glühen, Härten und Anlassen d. Metalle auf  
Grund d. physik. u. chem. Eigenschaften. Dresden: Gustav Wolf. 63 pp. M 25.

**WILST, FRITZ and DURRER, ROBT:** Temperatur-Warmeinhaltskurven wichtiger  
Metall-Legierungen. Berlin: Verlag d. Vereines Deutscher Ingenieure. 46 pp. M 38.

**Mineral separation by flotation.** R. LUCKENBACH. U. S. 1,417,261, May 23.  
A frothing agent is prepd. from rosin pitch, NaOH and  $H_3BO_3$ . U. S. 1,417,262 relates  
to a frothing agent prepd. from alkali and alc. U. S. 1,417,263 relates to a frothing  
agent from alkali and a normally unsaponifiable resin which may be used with Na oleate.

**Reagent for concentration of ore by flotation.** R. LUCKENBACH. Can. 219,757,  
June 20, 1922. Rosin pitch or the product of reaction of rosin pitch and an alkali is  
mixed with finely divided ore and water; the pulp is aerated and the froth removed.

**Reducing ores.** W. E. TRENT. Can. 219,183, May 30, 1922. Finely divided  
Fe or other ores are mixed with a carbonaceous fuel freed of hydrocarbons and heated  
in a reducing atm. The ore may be mixed with pulverized coal and indirectly heated  
to partial reduction and removal of volatile matter from the coal. The impurities of the  
ore and the non-carbonaceous matter in the coal are removed and the ore is reduced by  
heating with the purified carbonized particles in a reducing atm. Cf. C. A. 15, 1876.

**Purifying and collecting ore.** W. E. TRENT. Can. 219,184, May 30, 1922. A  
hydrocarbon oil and comminuted carbonaceous matter are mixed with the ore in water,  
the mixt. is agitated to agglomerate the mineral, carbonaceous material and oil sub-  
stantially free from froth, water and impurities. Cf. C. A. 15, 2411.

**Roasting sulfide ores.** P. R. MIDDLETON and J. C. LALOR. Can. 219,153, May  
30, 1922. Sulfide ores are heated with access of air to a temp. below the ignition point  
of S, this temp. is maintained till the max. proportion of the sulfide is oxidized to sulfate  
and then a portion only of the sulfate is decomposed to establish the desired acid-balance  
in electrolysis.

**Treating gold or silver ore containing manganese.** M. F. FAIRLIE and J. J. DENNY.  
U. S. 1,417,153, May 23. Au or Ag ore contg. an oxide of Mn is first treated with Fe  
and  $H_2SO_4$  in order to react with the  $MnO_2$  and the sepd. ore is then cyanided.

**Flux for ores.** B. F. PYLE. U. S. 1,416,871, May 23. A mixt. of soda, potash,  
fluorite, NaCl,  $SiO_2$ , charcoal, coke, graphite and "carbon" is used in smelting ores  
such as those of Zn, Cu, W, U, V or Al.

**Apparatus for electric ore concentration.** J. B. MCCARTHY. U. S. 1,417,189,  
May 23.

**Ore-concentrating apparatus.** J. B. ARTHUR. U. S. 1,416,928, May 23.

**Treating copper sulfide ores.** N. V. HYBINETTE. U. S. 1,407,420, Feb. 21.  
See Can. 216,249 (C. A. 16, 1388).

**Desulfurizing iron ores.** WM. L. ESTABROOKE. Can. 219,660, June 20, 1922.  
Elementary halogen or a halogen compd. which is volatile at the working temp. is intro-  
duced into the material to be desulfurized to form a S halide. This passes off through  
the stack and may be condensed.

**Extraction of lead zinc sulfide ores.** J. J. COLLINS. Can. 219,168, May 30, 1922.  
Powdered ore is introduced into a soln. of the lower chloride of a metal having 2 valencies

and Cl gas is passed into the soln. to form  $PbCl_2$ , while the ZnS remains unattacked. The soln. is drawn off and the solid residue treated with a hot satd. soln. of NaCl to dissolve the  $PbCl_2$ , leaving the ZnS and S. Any Ag may be recovered from the residue.

**Copper extraction from its ores.** A. A. LOCKWOOD. Can. 218,987, May 23, 1922. Reissue of 191,091. See C. A. 13, 98.

**Furnace for the production of mineral distillates.** H. MAYERS. Can. 219,508, June 13, 1922.

**Feeding pulverized coal to a blast furnace.** E. H. HAMILTON and L. W. KIRK. Can. 219,655, June 13, 1922. A stream of pulverized coal is delivered into the main air blast at substantially the point where the latter enters the interior of the furnace. App. is specified.

**Gas-discharge conduit for rotary converters.** W. H. HOWARD. Can. 219,392, June 6, 1922.

**Gas-fired furnace for melting alloy steels.** J. A. GASKILL. U. S. 1,417,478, May 23.

**Gas-fired furnace adapted for heat-treating steel gears.** W. C. PETERSON. U. S. 1,418,746, May 23.

**Detinning iron.** J. S. MORGAN. Can. 219,558, June 13, 1922. Iron coated with Sn is treated with an anti-flux, such as NaOH, at a temp. above the m. p. of Sn, while the material is being passed through the surface of a molten metal, such as Sn or Pb, with which the anti-flux does not mix and which is at a temp. above the m. p. of Sn.

**Iron and steel.** H. LANG. Can. 219,499, June 13, 1922. Finely ground Fe ore and a reducing agent are packed in iron containers, each having a porous closure, then subjected to a reducing temp. and finally melted without exposing to the atm. App. is also specified. The packed iron containers, after the reducing operation, may be used as electrodes in an elec. melting furnace.

**Steel and high-phosphorus slag.** WM. R. WALKER. Can. 219,510, June 13, 1922. Ore is smelted to form pig Fe, which is desiliconized without substantially reducing the percentage of P, and the metal is refined with a basic slag. The slag is removed before the end of the refining operations and when it contains the greater part of the P to be extd.

**Welding cast iron to steel.** J. F. R. ROUSSEAU. U. S. 1,416,879, May 23.

**Chromium alloys.** B. M. S. KALLING. Can. 219,811, June 20, 1922. A Cr alloy contg. more than 10% Si, in the presence of substances capable of dissolving  $SiO_2$  and substances contg. compds. of Cr and O, is subjected to the action of air blown through the molten alloy.

**Zinc-aluminium alloy.** A. U. RANDALL. U. S. 1,417,348, May 23. An alloy of Zn 84 and Al 16% is adapted for the manuf. of bearings.

**Solder.** G. P. LUCKEY. Can. 218,653, May 16, 1922. A solder contg. Pb 90-94% and Cd 10-6% begins to melt at  $249^\circ$  and is completely melted at  $280^\circ$ .

**Soldering composition.** A. TRALIOT. U. S. 1,417,428, May 23. A compn. for soldering Al or cast Fe is formed of Al, Sn, Pb and S in equal amts.

**Solder for aluminium.** F. A. ALBERTUS. U. S. 1,416,924, May 23. The solder is formed of Sn 58.45, Zn 35, Al 4.19, Sb 1.22 and phosphor-Sn 1.14 parts.

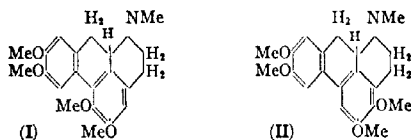
**Heat-treating sheet and tinplate bars.** T. V. ALLIS. U. S. 1,417,012, May 23. Mechanical features.

## 10—ORGANIC CHEMISTRY

CHAS. A. ROULLER

**Laurotetanine, the tetanizing alkaloid of various lauraceae.** K. GORREX. *Bull. jard. bot. Buitenzorg* (iii) 3, 180-98(1921); cf. Greshoff, *Ber.* 23, 3537-50; Filippo,

*Arch. Pharm.* **236**, 601-22 (1898).—G. prepd. laurotetanine (B) in a yield of 0.38%, from the bark of *Laisen cubeda*, Pers.; it probably occurs in some dozen other Lauraceae,  $[\alpha]_D^{25}$  98.5°. The moist alkaloid crystd. from acetone m. 125° (not 134° as indicated by Filippo). It has the compn.  $C_{11}H_{11}O_4N$  (Filippo), but loses 0.5 H<sub>2</sub>O in a vacuum over H<sub>2</sub>SO<sub>4</sub> and a second 0.5 H<sub>2</sub>O at 80° over P<sub>2</sub>O<sub>5</sub>, so that the anhydrous alkaloid is  $C_{11}H_{10}O_4N$ . It is a phenolic base, readily oxidizes, and is colored yellow, but withstands electrolytic reduction. The compn. of laurotetaninephenylthiocarbamide, NHPhCSNHC<sub>11</sub>H<sub>10</sub>O<sub>4</sub>N, m. 211-2°, confirms the anhyd. formula. Laurotetanine hydrobromide,  $C_{11}H_{10}O_4N \cdot HBr$ , crystals with 6, the hydriodide with 5, the sulfate,  $B_2 \cdot H_2SO_4$ , with 12 and 5, the picrate, m. 148°, with 1.5 H<sub>2</sub>O. *Dibenzoyllaurotetanine* m. 169-70°; Filippo's compd. was probably the mono-*N*-Bz deriv. Nascent CH<sub>2</sub>N<sub>2</sub> (from ONCMeCO<sub>2</sub>Me) methylates only the single OH group, forming *laurotetanine methyl ether*, amorphous, insol. in NaOH, and yielding a cryst. *sulfate, hydrochloride*,  $C_{11}H_{10}O_4N \cdot HCl \cdot 1.5H_2O$ , m. 245°, *oxalate*,  $B_2 \cdot C_2H_2O_4$ , m. 233°, and *thiocarbamide*, m. 154-5°. On the other hand, preformed CH<sub>2</sub>N<sub>2</sub> in Et<sub>2</sub>O furnishes *N-methylaurotetanine methyl ether (isoglaucine)*,  $C_{11}H_{10}O_4N \cdot 3H_2O$ , m. 63°,  $[\alpha]_D^{27}$  109°; this base sublimes unchanged in a vacuum. It is isomeric with glaucine (cf. Gadamer, *C. A.* **6**, 2140), which it resembles closely in optical rotation, color reactions, and pharmacological properties. *Isoglaucine, hydrochloride*, crystals with 2 and with 5H<sub>2</sub>O and m. anhyd. 239°, the *hydrobromide* m. 252°; the *l-hydrogen tartrate*,  $C_{11}H_{10}O_4N \cdot C_4H_2O_6 \cdot 3H_2O$ , loses 2H<sub>2</sub>O in a vacuum over P<sub>2</sub>O<sub>5</sub> at 80°, the rest at 110°. The *methiodide* m. 229°. These salts differ from the corresponding salts of glaucine.



According to G., the difference between glaucine (I) and isoglaucine (II) must lie in the orientation of the MeO groups. Formula I was established synthetically by Gadamer, who states that the color reactions are due to unsubstituted 1,4-positions in the ring on the extreme left of the above formula. As these reactions are shared by isoglaucine, G. concludes the difference is in the lowest ring. By oxidation of laurotetanine with alk. KMnO<sub>4</sub>, he has obtained 1,2,3,4,5-C<sub>6</sub>H(OMe)<sub>2</sub>(CO<sub>2</sub>H)<sub>3</sub>, which must be derived from the lowest ring, since this is the only one attached to three C atoms. At the same time, it follows that the two MeO groups of this ring are equally in *o*-positions in isoglaucine, so that the only way in which (on the above suppositions) a difference from glaucine can be expressed is by formula II. J. C. S.

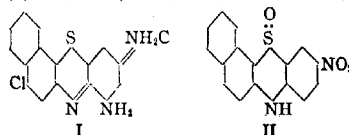
**Linear (benzonaphtho)-parathiazines.** K. FRIES AND F. KERKOW. *Ann.* **427**, 281-302 (1922).—2-Anilino-3-methylmercapto-1,4-naphthoquinone results by the action of Na<sub>2</sub>S followed by Me<sub>2</sub>SO<sub>4</sub> on the corresponding 3-Cl deriv., and forms long, violet needles, m. 143°. If the intermediate 3-mercapto derivative is acidified and the ppt. oxidized with air in boiling alc., *lin*-(benzonaphtho)-parathiazine-5,10-quinone (A) is formed, compact, steel-blue crystals, m. 308°. The concd. H<sub>2</sub>SO<sub>4</sub> soln. is olive-green. H<sub>2</sub>O<sub>2</sub> in AcOH gives the *sulfoxide*, red, does not m. 360°; it is amphoteric, dissolving in warm NaOH with deep red and in dil. acids with yellow color. Warmed with a larger amt. of H<sub>2</sub>O<sub>2</sub>, A gives the *sulfone*, compact, orange-red crystals, m. above 360°; from PhNO<sub>2</sub>, golden leaflets. The soln. in concd. H<sub>2</sub>SO<sub>4</sub> is blood-red. *Sodium salt*, red needles with 1 H<sub>2</sub>O. Heated for a few min. with concd. HCl in AcOH, the 2-chloro derivative of A is formed, compact, blue needles from PhNO<sub>2</sub>, m. 303°. 2-Bromo derivative,



steel-blue needles, m. 309°. *N-Methyl derivative*, formed by the action of  $\text{Me}_2\text{SO}$  upon a mixt. of A and  $\text{MgO}$ , bluish needles, m. 197°. Reduced with  $\text{ZnCl}_2\text{-AcOH}$ , A gives 5,10-dihydroxy-[lin-(benzonaphtho)-parathiazine], (B), darkens 180°, m. 192°. *Diacetate*, Ag-like leaflets, m. 258°. *Dimethyl ether*, by reduction of A with hyposulfite followed by  $\text{Me}_2\text{SO}$  treatment, large, pale yellow monoclinic tables, m. 134°. *Concd.  $\text{H}_2\text{SO}_4$* , gives a blue-violet color. The action of  $\text{ClCO}_2\text{Et}$  upon B gives a compound,  $\text{C}_{20}\text{H}_{15}\text{O}_3\text{NS}$ , yellow needles, m. 203° (decompn.). An excess of  $\text{ZnCl}_2$  and A, warmed for 1 hr., gives lin-(benzonaphtho)-parathiazine, large yellowish, transparent leaflets, or needles m. 277°. 2-[p-Aminoanilino]-3-chloro-1,4-naphthoquinone, from the 2,3- $\text{Cl}_2$  deriv. and p- $\text{C}_6\text{H}_4(\text{NH}_2)_2$ , blue-violet, m. above 360°. *Acetate*, by using  $\text{AcNHC}_6\text{H}_4\text{NH}_2$ , purple-red prisms, m. 271° (decompn.). 3-Methylmercapto derivative, indigo-blue crystals, m. 243°. 2-Acetamino-[lin-(benzonaphtho)-parathiazine]-5,10-quinone, by oxidation of the mercapto derivative in alc. with air, fine, green needles, m. about 340° (decompn.). *Sulf oxide*, brownish red powder, decomp. 330°. *Sulfone*, brownish red, compact needles, does not m. 360°. 2-Amino derivative, by heating the acetate with 150 parts (1:1)  $\text{H}_2\text{SO}_4$  1 hr., green powder, m. about 290°. Its salts are blue; the soln. in alc. KOH is yellow. 2-Acetamino-5,10-dihydroxy-[lin-(benzonaphtho)-parathiazine] (C), isolated as the hydrochloride; diacetate, glistening plates, decomp. 257°. 2-Amino-[lin-(benzonaphtho)-parathiazine] hydrochloride, by the continued action of  $\text{ZnCl}_2$  upon C, pale olive-green crystals, which darken in the air; the free base forms a green powder, decomp. 280°. *Acetate*, greenish yellow crystals, decomp. 285°. lin-(Benzonaphtho)-2-thiazine-bluish black crystals, decomp. 290°.

C. J. WEST

Synthesis of oxazines and thiazines of the naphthalene series. ZDENKA LUDWIG-SEMELEC. *Rev. chim.* 1, 84-8, 129-36(1921).—A continuation of a paper of which part has already appeared (cf. C. A. 15, 3976). Other methods of prep.  $\beta,\alpha$ -naphthophenoxazine-5-anil, orange-yellow crystals, m. 216°, are (a) fusion of 2-hydroxy-1,4-naphthoquinone monoanil with o- $\text{HOC}_6\text{H}_4\text{NH}_2\cdot\text{HCl}$  (A), and (b) oxidation of the crude product obtained by fusing 1,2- $\text{C}_{10}\text{H}_6(\text{OH})_2$  with A by means of  $\text{FeCl}_3$  in the presence of aniline. It forms a hydrochloride, red needles with a green, metallic reflex and a chloroplatinate,  $(\text{C}_{22}\text{H}_{16}\text{ON}_2\text{Cl})_2\text{PtCl}_6$ , small, dark brown crystals. 5-Chloro-8,10



diamino- $\alpha,\beta$ -naphthophenothiazonium chloride (I), dark blue needles, and 10-nitro- $\alpha,\beta$ -naphthophenothiazine S-oxide (II), small, orange-yellow needles, are obtained from the product of nitrating  $\alpha,\beta$ -naphthophenothiazine as previously described (C. A. 15, 3976).

J. C. S.

Natural system of the carbon compounds. II. Empirical and rational allologic series and their graphical representation as a system. HERMAN DEKKER. *Helvetica Chim. Acta* 5, 285-99(1922); cf. C. A. 16, 1929.—All series of hydrocarbons in which a const. difference exists between members are classed as "allologic series." In this classification are series whose members correspond in this const. difference, but are dissimilar from the standpoint of structural chemistry. Homologous series are subdivided into 3 parts. *Empirical homologs* are those having a const. difference of  $\text{CH}_2$  or a multiple thereof. This definition does not involve structure, and only includes those compds. derived from a fundamental hydrocarbon. *Rational homologs* are compds. of definite structural formula which become either by the addn. or by the removal of  $\text{CH}_2$ , a higher or a lower member, resp. *Irrational homologs* differ by  $\text{CH}_2$  or a multiple

thereof, but cannot be converted into one another by addn. or removal of this group. The members of paraffin series are rational homologs of  $\text{CH}_4$ , but in the  $\text{C}_n\text{H}_{2n-2}$  series the acetylene and allylene compds. are not derived from one another. In the aromatic series, cases of irrational homology are numerous, such as  $\text{C}_{18}\text{H}_{10}$  and  $\text{C}_{18}\text{H}_{14}$  of the  $\text{C}_n\text{H}_{2n-2}$  group which exhibit no rational homology. An aryl compd. cannot belong to a rational homologous series because it contains no primary or secondary C atom. The allologic series  $\text{C}_8\text{H}_8$ ,  $\text{C}_{10}\text{H}_8$ ,  $\text{C}_{14}\text{H}_{10}$ , ... and  $\text{C}_{12}\text{H}_{10}$ ,  $\text{C}_{16}\text{H}_{12}$ ,  $\text{C}_{20}\text{H}_{14}$ , ... are of the general formula  $\text{C}_n\text{H}_{(n+K)/2}$  where  $K$  is a sp. const. of this benzologic series, varying by 2 from series to series. Similarly for the phenylogic series  $\text{C}_6\text{H}_6$ ,  $\text{C}_{12}\text{H}_{10}$ ,  $\text{C}_{18}\text{H}_{14}$ , ... and for the perillogic series  $\text{C}_{16}\text{H}_8$ ,  $\text{C}_{16}\text{H}_{10}$ ,  $\text{C}_{22}\text{H}_{12}$ , ... the general formulas are  $\text{C}_n\text{H}_{(2n+K')/3}$  and  $\text{C}_n\text{H}_{(n+K'')/3}$ , resp. An allologic series can be expressed in arithmetical terms and thus be converted to a geometric basis. The C and H of any compd.  $\text{C}_n\text{H}_m$  can be expressed by the equation  $n + K_1m + K_2 = 0$ , i. e., paraffins  $n - (m/2) + 1 = 0$ , acetylenes  $n - (m/2) - 1 = 0$ , benzene  $n - (m/2) - 3 = 0$ , diphenylphenylnaphthalenes  $n - 2m + 8 = 0$ , etc. With coordinates  $n$  and  $m$  the various series are shown graphically. The great no. of hydrocarbons still unknown is thus emphasized. For aryl compds., the equation  $R = (n - m)/2 + 1$  gives the no. of rings (R) in any compd.

C. C. DAVIS

Action of the dichloro ether  $\text{CH}_2\text{ClCHClOEt}$  on the magnesium derivative of allyl bromide. R. LESPIEAU. *Bull. soc. chim.* 31, 412-4 (1922).—Mg turnings suspended in  $\text{Et}_2\text{O}$  were treated alternately with small quantities of  $\text{C}_3\text{H}_7\text{Br}$  and di-Cl ether, the  $\text{Et}_2\text{O}$  was evapd. off and the residue distd. with steam. The product consisted of diallyl and a considerable amt. of high boiling substances, and a fraction, b.  $156-7^\circ$ , which was a mixt. of  $\text{CH}_2\text{ClCH}(\text{OEt})_2$  and 5-chloro-4-ethoxy-1-pentene, b.  $158-8.5^\circ$ ,  $d_{17}$  0.967. The latter was sepd. by prepg. the Br addition product 5-chloro-4-ethoxy-1,2-dibromopentane,  $b_{13}$   $143-4^\circ$ ,  $d_{25}$  1.63, then removing the Br with Zn and  $\text{EtOH}$ . Yield, only 3%.

A. W. DOX

Labile nature of the halogen atom in organic compounds. I. Titanium reductions of substituted nitroparaffins. THOMAS HENDERSON AND ALEX. K. MACBETH. *J. Chem. Soc.* 121, 892-903 (1922); cf. *C. A.* 15, 1501.—The results of the reduction expts. may be summarized as follows:  $\text{C}(\text{NO}_2)_4$ : one  $\text{NO}_2$  group is readily removed by  $\text{TiCl}_3$ ,  $\text{N}_2\text{H}_4$ ,  $\text{K}_4\text{Fe}(\text{CN})_6$ ,  $\text{K}_2\text{SO}_3$ , etc.  $\text{TiCl}_3$  further reduces to  $(\text{NH}_2)_2\text{C} : \text{NH}$  the  $\text{HC}(\text{NO}_2)_3$  initially produced.  $\text{KOH}$  also removes one  $\text{NO}_2$  group, giving the aci-K salt of  $\text{HC}(\text{NO}_2)_3$ .  $\text{ClC}(\text{NO}_2)_3$  and  $\text{BrC}(\text{NO}_2)_3$ : The halogen atom is readily removed by alk. reducing agents and by  $\text{K}_4\text{Fe}(\text{CN})_6$ .  $\text{TiCl}_3$  also splits off the halogen atom and then reduces the  $\text{NO}_2$  groups,  $(\text{NH}_2)_2\text{C} : \text{NH}$  being produced  $\text{Br}_2\text{C}(\text{NO}_2)_2 : \text{N}_2\text{H}_4$ ,  $\text{K}_4\text{Fe}(\text{CN})_6$ , or  $\text{KOH}$  removes one of the Br atoms.  $\text{TiCl}_3$  reduces the  $\text{NO}_2$  groups but leaves the halogen unattacked.  $\text{Cl}_3\text{CNO}_2 : \text{N}_2\text{H}_4$  removes 1 of the Cl atoms very slowly in the cold.  $\text{K}_4\text{Fe}(\text{CN})_6$  is without action.  $\text{TiCl}_3$  reduces the  $\text{NO}_2$  group, but does not attack the halogen.  $\text{BrCH}_2\text{NO}_2$  and  $\text{Br}_2\text{CHNO}_2 : \text{TiCl}_3$  reduces the  $\text{NO}_2$  group but does not remove the halogen.  $\text{N}_2\text{H}_4$  and  $\text{K}_4\text{Fe}(\text{CN})_6$  are without action.  $\text{ClC}_2\text{H}_2(\text{NO}_2)_2$  gives  $\text{C}_2\text{H}_2(\text{NH}_2)_2$  by the action of  $\text{TiCl}_3$ .  $\text{BrC}(\text{NO}_2)_3$ , acting on a dil.  $\text{HBr}$  soln. of  $\text{PhOH}$ , gave  $\text{Br}_2\text{C}_6\text{H}_4\text{OH}$ . From this work it seems clear that the halogen-substituted nitroparaffins are no longer to be considered as an isolated class, since, when considered from the point of view of the alternate effect in a chain, their chief reactions may be correlated with the chem. properties of substances of a very diverse type. There are strong grounds for accepting the existence of some force (electrical or otherwise) in the mol. since the application of the view is so fruitful in explaining chem. changes over a very wide field.

II. Action of hydrazine on nitrogen-halogen compounds and on bromomalonate esters. E. L. HIRST AND A. K. MACBETH. *Ibid.* 904-11; cf. *C. A.* 15, 3980.—The previous work has been extended to a large no. of N-halogen compds. It is shown that they all react

with  $N_2H_4$ , the N being evolved immediately and quant.  $BrCH(CO_2X)_2$  and  $Br_2C(CO_2X)_2$  also react quickly with  $N_2H_4$ , the liberation of N extending only over 1 min. The substituted esters also react but the time required for complete reduction is longer and increases as substitution proceeds. In some cases 2-3 hrs. are required to complete the reaction. The results are slightly low and may be due to incomplete reaction. The decreased rate of reaction may be due to steric hindrance, since the result with  $BrCAg(CO_2Et)_2$  was intermediate between that for  $BrCH(CO_2Et)_2$  and that for  $BrCMe(CO_2Et)_2$ .  $O_2NCH(CO_2Et)_2$  did not react but  $BrC(NO_2)(CO_2Et)_2$  reacted with quant. removal of the Br.

C. J. WESSER

**The chlorites of ammonium, of tetramethylammonium and of some amines.** G. R. LIGVI. *Gass. chim. ital.* 52, 1, 207-9(1922).—This paper is a continuation of one previously published with Bruni (C. A. 10, 1820). Pure  $Ba(ClO_3)_2$  with mol. amts. of  $(NH_4)_2SO_4$  in concd. solns. at 15-20° gave a filtrate which, evapd. *in vacuo* over  $CaCl_2$ , gave ammonium chlorite,  $NH_4ClO_2$ , as long faintly yellow transparent needles. Excess  $SO_3$  reduces  $NH_4ClO_2$  to  $NH_4Cl$ . Cl was detd. in this way. A 30 % soln. of  $NH_4Me$  neutralized with 2 N  $H_2SO_4$  and treated with  $Ba(ClO_3)_2$ , etc., as above gave a dense soln. containing 66 % monomethylamine chlorite,  $NH_2Me.HClO_2$ , which could not be crystd. This concd. soln. poured on a plate of cold Fe gives a slight explosion. Dimethylamine chlorite,  $NHMe_2.HClO_2$ , was obtained similarly and was also decompd. by heat. Trimethylamine chlorite,  $NMe_3.HClO_2$ , was obtained similarly and underwent decompn. even more easily. The soln. obtained from equimol. amts. of  $(NMe_3)_2SO_4$  and  $Ba(ClO_3)_2$  was evapd. *in vacuo* as above and gave colorless crystals of tetramethylammonium chlorite.  $NMe_4ClO_2$ , which explodes on percussion unlike  $NH_4ClO_2$ , is deliquescent and reacts neutral in aq. soln.

E. J. WITZEMANN

**The systematic extension of the preparation of organo-metallic compounds. Application to ferrous ethyl iodide.** A. JOB AND R. REICH. *Compt. rend.* 174, 1358-61 (1922).—From numerous expts. on the reactions of organo-Zn compds. with anhyd. chlorides of several metals, the conclusion is drawn that any metal may form substances similar to the Grignard compds. The failure of many earlier attempts to substitute other metals for Mg by interaction of metal halides with  $RMgX$  is held to be due to the too great reactivity of the Mg derivs. In the synthesis of  $EtFeI$ , an  $Et_2O$  soln. of  $FeI_2$  is first prepd. by agitating an excess of reduced Fe with a mixt. of I and anhyd.  $Et_2O$ ; 100 cc. of the mixt., containing 0.1 mol.  $FeI_2$ , is filtered, out of contact with air by means of  $CO_2$  pressure, into a reaction flask and treated with 50 cc. (0.1 mol.) of  $EtZnI$  in  $Et_2O$ ; the reaction, at the b. p. of  $Et_2O$ , is complete in 6 hrs. The reaction  $EtZnI + FeI_2 \rightarrow EtFeI + ZnI_2$  is shown to have taken place by treatment of the mixt. with  $H_2O$  and detn. of the  $C_2H_6$  and  $Fe(OH)_2$  thus formed. In the course of the substitution reaction, portions of the mixt. treated with  $H_2O$  show progressive diminution in the proportion of  $Zn(OH)_2$  and increase in the amt. of  $Fe(OH)_2$  formed. The  $Et_2O$  soln. of  $EtFeI$  reacts in a manner analogous to that of  $EtZnI$ ; thus with abs.  $EtOH$  it forms ethane and  $EtOFeI$ .  $FeCl_3$  is instantly and quant. reduced to  $FeCl_2$  by  $EtZnI$  according to the equation  $2FeCl_3 + EtZnI \rightarrow 2FeCl_2 + EtI + ZnCl_2$ ; the  $FeCl_2$  then reacts with excess  $EtZnI$  giving  $EtFeCl$ .  $Cu_2Cl_2$  was found to substitute Cl for I in  $EtZnI$ . The work is being extended to the Ph series, and to mixed derivs.

A. R. ALBRIGHT

**Elimination of carbon dioxide from organic compounds. IV. Fission of chloral hydrate by mercury acetate, mercury oxide, and certain other metallic oxides.** H. KUNZ-KRAUSE AND P. MANICKE. *Ber. pharm. Ges.* 31, 233-9(1921); cf. C. A. 14, 2635.— $MgO$  and the oxides of Hg, Zn and Cu react with  $CCl_3CH(OH)_2$  in a similar manner to that of the alkali and alk. earth metals in so far as  $CHCl_3$  results independently of the chem. character of the metallic ion involved. There is this difference, however,

in that the  $\text{CH}_3\text{O}_2$  simultaneously formed remains as formate in the case of the alkali and alk. earth hydroxides, while with  $\text{MgO}$  and the oxides of the heavy metals, decompn. of the formate into  $\text{CO}$  and  $\text{CO}_2$  takes place. For equations representing the main reactions involved with  $\text{HgO}$  cf. *C. A.* 16, 987.

W. O. F.

**Method of pyrogenic decomposition, at a high temperature, of acetone. (MILLER.)**  
ÉGLANTINE PEYTRAL. *Bull. soc. chim.* 31, 122-4 (1922).—Acetone from its bisulfite compd. when passed rapidly through a Pt tube at about  $1100^\circ$  split almost entirely into  $\text{CH}_3\text{CO}$  and  $\text{CH}_4$ , these further decomposing into  $\text{CO}$  and  $\text{C}_2\text{H}_4$ . Passed at slower rates small amts. of  $\text{AcH}$  result which decomposes into  $\text{CO}$  and  $\text{CH}_4$ .

B. V. B.

**Spontaneous condensation of ethoxyacetone; formation of 1,5-diethoxy-2-methyl-2-pentanol-4-one. VICTOR DAUDEL.** *Bull. soc. chim.* 31, 265-8 (1922).—Ethoxyacetone on long standing undergoes a spontaneous condensation similar to the aldol condensation and forms 1,5-diethoxy-2-methyl-2-pentanol-4-one.

R. C. R.

**Method of pyrogenic decomposition, at high temperatures, of methyl acetate. (MILLER.)** ÉGLANTINE PEYTRAL. *Bull. soc. chim.* 31, 118-22 (1922).— $\text{MeOAc}$  when passed at a comparatively rapid rate through a Pt tube at about  $1100^\circ$  decompd. to form, 1st,  $\text{AcH}$  and  $\text{HCHO}$ ; 2nd,  $\text{AcOH}$  and  $\text{C}_2\text{H}_4$ ; the  $\text{AcH}$  decompd. into  $\text{CH}_4$  and  $\text{CO}$ ,  $\text{HCHO}$  into  $\text{H}$  and  $\text{CO}$ ;  $\text{AcOH}$  into  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}$  and  $\text{C}_2\text{H}_4$ . When it was passed at slower rates the gaseous products increased and some graphite was formed.

B. V. BUSH

**Nitro- and aminoglycols. II. ERICH SCHMIDT AND RUDOLF WILKENDORF.** *Ber.* 55B, 316-22 (1922); cf. *C. A.* 13, 2361.— $\beta$ -Chloro- $\beta$ -nitrotrimethyleneglycol (2-chloro-3-nitropropane-1,3-diol) (A), obtained quant. from dry  $\text{O}_2\text{NCNa}(\text{CH}_2\text{OH})_2$  in cold  $\text{Et}_2\text{O}$  treated with  $\text{Cl}$  until a sample of the suspended salt, filtered and washed with  $\text{Et}_2\text{O}$ , no longer carbonizes on a Pt foil but leaves only  $\text{NaCl}$ , forms stout prisms, m.  $115-6^\circ$ , gives with  $\text{BzCl}$  in quinoline after 2.25 hrs. on the  $\text{H}_2\text{O}$  bath the dibenzoate, m.  $114-5^\circ$ .  $\text{O}_2\text{NCH}(\text{CH}_2\text{OH})_2$  is obtained in 10.5 g. yield from 15.6 g. A in 80 cc.  $\text{H}_2\text{O}$  and 10 g.  $\text{C}_6\text{H}_5\text{N}$  shaken with 1.5 g. palladinized  $\text{BaSO}_4$  and  $\text{H}$ , filtered, treated with 25 g. crystd.  $\text{KHSO}_4$  and exhd. 40 hrs. in a Kempf app. with  $\text{Et}_2\text{O}$ . 1-Nitro-1-nitro-2-propanol is obtained in 98.4% yield from  $\text{MeCH}(\text{OH})\text{CH}_2\text{NO}_2$  in cold alc. slowly treated with 1.3 atoms  $\text{Na}$  in alc. and allowed to stand 2-3 hrs. in ice; in  $\text{Et}_2\text{O}$  with  $\text{Cl}$  it gives 70% 1-chloro-1-nitro-2-propanol, b<sub>11</sub>  $91-2^\circ$ , becomes faintly yellow on long standing, gives when added to 1.5 mols. aq.  $\text{AcH}$  and made faintly alk. to litmus with  $\text{KOH}$  68% of 3-chloro-3-nitropentane-2,4-diol (B), b<sub>0.5</sub>  $109-12^\circ$ , as a viscous oil solidifying in 2-3 days and sepg. from 1 : 1  $\text{CHCl}_3\text{-CCl}_4$  in needles m.  $118-9^\circ$ ; dibenzoate, m.  $115-60^\circ$ . 3-Nitropentane-2,4-diol (7 g. from 18.4 g. B in  $\text{H}_2\text{O-C}_6\text{H}_5\text{N}$  with  $\text{H}$  and palladinized  $\text{BaSO}_4$ ), b<sub>0.5</sub>  $109-10^\circ$ , slowly depositing crystals (2.9 g.), m.  $68-9^\circ$ , gives in  $\text{H}_2\text{O}$  with  $(\text{CO}_2\text{H})_2$ , palladinized  $\text{BaSO}_4$  and  $\text{H}$  70-80% of 3-aminopentane-2,4-diol oxalate,  $\text{C}_5\text{H}_{11}\text{O}_4\text{N}_2$ , decomp.  $178-9^\circ$ .

C. A. R.

**The acid aldehydes of the succinic series. E. CARRIÈRE.** *Ann. chim.* 17, 38-132 (1921).—The object of the work was to study a general method for prepg. aldehyde acids, certain of which have been prepd. in small yield by Harries and Tank (*C. A.* 2, 2375) who decompd. ozonides with  $\text{H}_2\text{O}$  (also *C. A.* 3, 183, and *Ann.* 343, 359 (1905)). These compds. have also been found among the oxidation products of unsatd. acids (*Ann.* 143, 34 (1867); 140, 66 (1866); *Ber.* 34, 1500 (1901); *Bull. soc. chim.* [3] 31, 161 (1904); *Ber.* 33, 2763 (1900)). Perkin and Sprankling prepd.  $\text{HO}_2\text{C}(\text{CH}_2)_2\text{CHO}$  (A) by condensing  $\text{CHNa}(\text{CO}_2\text{Et})_2$  with  $\text{MeCBr}(\text{OEt})_2$  (*J. Chem. Soc.* 75, 16 (1899)). Frankenstein (*Diss. Koenigsberg* 1899), and von Ungern Sternberg (*Diss. Koenigsberg* 1904) prepd. A by decomp. aconic acid (B) with  $\text{H}_2\text{O}$ . Homologs of A cannot be prepd. by this method because homologs of B are not known. Harries and Alefeld formed A in 10% yield by decomp. the ozonide of allylacetic acid with  $\text{H}_2\text{O}$ .  $\text{OHCCH}(\text{CO}_2\text{Et})\text{CH}_2\text{CO}_2\text{Et}$  (F) was prepd. by Wislicenus, Boklen and Reuthe (*C. A.* 3, 790) by condensing

$\text{HCO}_2\text{Et}$  (C) with  $\text{EtO}_2\text{CCH}:\text{CHCO}_2\text{Et}$  (D) but C. found that  $\text{NaOEt}$  gave good results. To 27.6 g. Na as  $\text{NaOEt}$  was added in small amts. 174 g. D with 89 g. C and after the mixt. stood in the cold for several days.  $\text{OHCCH}(\text{CO}_2\text{Et})\text{CHNaCO}_2\text{Et}$  (E) sepd. It was then

treated with  $\text{H}_2\text{SO}_4$ , extd. with  $\text{Et}_2\text{O}$  and the calcd. amt. of F,  $b_{14}$  128–148°, was obtained. The range is wide because of the presence of the enolic and aldehyde forms. The Meyer technic was used for the study of the equil. (C. A. 8, 1774). The enolic form in F after standing several hrs. was 50% and in a 4.643% soln. in alc. fell to 12% at the end of 4 days. On distn. the first portion contained 30% of enolic F and the last portion 60%. All fractions at the end of several hrs. contained 50% enolic F and the sepn. could not be effected by distn. Ethyl formylsuccinate semicarbazone (CC), white crystals, m. 126°, and the *p*-nitrophenylhydrazone, yellow crystals, m. 100°. Et benzoylformylsuccinate was prepd. by condensing F with  $\text{BzCl}$ ,  $b_{14}$  208–12° (not in accord with the value given by W., R., and B.), needles m. 58–9°. The action of  $\text{PhNH}_2$  and certain of its derivs. on F was studied. From the product resulting when F interacted with  $\text{PhNH}_2$ , ethyl anilinoitaconate, yellow crystals, m. 102°, was obtained. Ethyl *p*-toluidinoitaconate (G) was prepd. in a similar manner. G sapond. with alc. KOH gave ethyl 1-*p*-cresyl-3-carboxylate-5-pyrrolinone (J),  $\text{MeC}_6\text{H}_4\text{N}:\text{CH}:\text{C}(\text{CO}_2\text{Et})\text{CH}_2\text{CO}$ , yel-

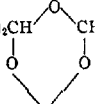
low crystals, m. 123–4°. Ethyl benzylaminoitaconate (H) was prepd. by treating F with  $\text{PhCH}_2\text{NH}_2$ , white crystals, m. 54°, and H when treated with alc. KOH followed by HCl gave ethyl 1-benzylamino-3-carboxylate-5-pyrrolinone, yellow crystals, m. 98°. J when sapond. by NaOH gave a small amt. of *p*- $\text{H}_3\text{NC}_6\text{H}_4\text{Me}$  and when the mixt. was treated with  $\text{H}_2\text{SO}_4$ ,  $\text{HCO}_2\text{H}$  and  $(\text{CH}_3\text{CO}_2\text{H})_2$  were formed.  $\text{NH}_4\text{OH}.\text{HCl}$  and  $\text{K}_2\text{CO}_3$  mixed with F gave ethyl formylsuccinate oxime (K), viscous liquid which on distn. gave ethyl  $\beta$ -cyanopropionate (L),  $b_{14}$  114–5°. L sapond. with KOH gave  $(\text{CH}_3\text{CO}_2\text{H})_2$ . Succinic acid aldehyde oxime,  $\text{HON}:\text{CHCH}_2\text{CH}_2\text{CO}_2\text{H}$ , white crystals, m. 155°. K when heated is dehydrated and the  $\text{H}_2\text{O}$  resulting from this action sapons. the ester group  $\beta$  to the CN group, the  $\text{CO}_2\text{H}$  group losing  $\text{CO}_2$  with formation of L. In prep.  $(\text{EtO}_2\text{C})_2\text{CHCHEtCO}_2\text{Et}$  (M)  $\text{EtCHBrCO}_2\text{Et}$  was first prepd. by the method of Hell, Volhard and Zelinsky and this was then condensed with  $\text{CHNa}(\text{CO}_2\text{Et})_2$ . The resulting tri-ester was sapond. by heating it 12 hrs. with HCl. The  $\text{H}_2\text{O}$  and HCl were eliminated *in vacuo* and the residue was heated in an oil bath at 150–60° to transform the carboxyethylsuccinic acid into  $\text{EtCH}(\text{CO}_2\text{H})\text{CH}_2\text{CO}_2\text{H}$  (N), of which a 78% yield was obtained (Ann. 192, 148(1878)). N was esterified to M, using alc. N, when heated with  $\text{AcCl}$ , gave  $\text{EtCH}.\text{CO}.\text{O}.\text{CO}.\text{CH}_2$  (O),  $b_{30}$  140° (Ann. 291, 121(1896)), which with  $\text{PhNH}_2$  in  $\text{C}_6\text{H}_6$

gave ethyl succinic acid amide (P), crystals from alc., m. 118°. P heated at 180° during 1.5 hrs. gave ethylsuccinic anil, crystals m. 74°. O heated 6 hrs. with  $\text{PCl}_5$  gave ethylsuccinyl chloride,  $\text{EtCH}(\text{COCl})\text{CH}_2\text{COCl}$ ,  $b_{14}$  94–5°, and when this compd. was treated with  $\text{PhNH}_2$  in  $\text{Et}_2\text{O}$  ethylsuccinic dianilide, crystals, m. 205°, was formed. Ethyl formylethylsuccinate (Q) was prepd. by treating  $\text{HCO}_2\text{Et}$  and M with  $\text{NaOEt}$  in  $\text{Et}_2\text{O}$  in the cold for 3 days.  $\text{H}_2\text{SO}_4$  was then added and Q sepd. and after treatment with  $\text{K}_2\text{CO}_3$  and distn. was obtained (88% yield) as an oil,  $b_{14}$  145–70°. The enolic form  $\text{HOCH}:\text{C}(\text{CO}_2\text{Et})\text{CHEtCO}_2\text{Et}$  and the aldehydic form  $\text{OHCCH}(\text{CO}_2\text{Et})\text{CHEtCO}_2\text{Et}$  exist and the equil. between these 2 forms as detd. by the Meyer technic was found to be attained slowly. An initial enol content of 37% fell to 17% in 3 weeks. The derivs. of the aldehydic form were the semicarbazone, white crystals from alc., m. 113°, the *p*-nitrophenylhydrazone, m. 113°, from  $\text{AcH}$ . The derivs. from the enolic form were the phenylurethan and the benzoate (the product reported as the phenylurethan was made by condensing Q with  $\text{BzCl}$  in  $\text{C}_6\text{H}_6\text{N}$ ,  $b_{14}$  220° ( $\text{C}_{14}\text{H}_{22}\text{O}_6$ ). ABSTR). Ethyl 1-phenyl-4-carboxylate-5-ethyl-6-pyridazinone,  $\text{EtCH}.\text{CO}.\text{NPh}:\text{N}:\text{CH}.\text{CHCO}_2\text{Et}$  (R),  $b_{14}$  225–40°

crystals from alc., was prepd. by heating Q with  $\text{PhNHNH}_2$ ; it was sapond. with NaOH to the free acid, crystals m.  $179^\circ$ . Q with  $\text{PhNH}_2$  gave a thick liquid, *ethyl anilinoethylitaconate*,  $\text{EtO}_2\text{CCHEtCH}(\text{:CHNHPH})\text{CO}_2\text{Et}$ , which when sapond. with alc. KOH followed by HCl treatment gave *1-phenyl-4-ethyl-3-carboxyl-5-pyrrolinone* (S),  $\text{Et}\cdot\text{CH}\cdot\text{CO}\cdot\text{NPh}\cdot\text{CH}\cdot\text{CCO}_2\text{H}$ , yellow crystals from alc. m.  $190^\circ$  (decompn.). Q interacted

with  $p\text{-MeC}_6\text{H}_4\text{NH}_2$  and the resulting ethyl *p*-toluidinoethylitaconate was sapond. with KOH, yielding *1-p-cresyl-4-ethyl-3-carboxyl-5-pyrrolinone* (T), yellow crystals from alc., m.  $203^\circ$ . S gave the corresponding ester when treated with alc. and HCl, crystals from alc., m.  $99^\circ$ , and T gave the corresponding ester, m.  $104^\circ$ . The equation for the transformation of F into A is:  $\text{F} + 2\text{H}_2\text{O} = \text{CO}_2 + \text{alc.} + \text{A}$ . A curve showing the rate of hydrolysis of F by  $(\text{CO}_2\text{H})_2$  is given, a max. being reached in 1 hr. The reaction was followed by the amt. of  $\text{CO}_2$  evolved. The  $(\text{CO}_2\text{H})_2$  was eliminated from the mixt. resulting from the hydrolysis by titration with  $\text{Ca}(\text{OAc})_2$ . The  $\text{Ca}(\text{C}_2\text{O}_4)$  was filtered and the ether ext. distd. *in vacuo* gave A,  $b_{18}$   $142\text{--}3^\circ$  (45% yield) (Harries and Alefeld gave  $b_{18}$   $134\text{--}6^\circ$ ; C. A. 3, 895).  $(\text{CH}_3\text{CO}_2\text{H})_2$  was also formed. According to the method of von Ungern Sternburg a 50% yield of A is obtained and the transformation of itaconic acid into B is only to the extent of 60%, whereas the transformation of  $(\text{CH}_3\text{CO}_2\text{Et})_2$  into F is quant. A gives with the Schiff reagent a violet color,  $\text{NH}_3\cdot\text{AgNO}_3$  is reduced at once in the cold as well as is Fehling soln. The semicarbazone m.  $194\text{--}5^\circ$  (decompn.) (H. and A. gave  $177\text{--}8^\circ$ ). The *p*-nitrophenylphenylhydrazone m.  $180\text{--}1^\circ$  (and not at  $175^\circ$ ; C. A. 3, 2154). The oxime, white crystals, m.  $102\text{--}3^\circ$ . *Naphthocinchoninylpropionic acid* was prepd. by dissolving  $\text{C}_{12}\text{H}_7\text{NH}_2$  in alc. with  $\text{AcCO}_2\text{H}$  and A and heating the mixt. 2 hrs., yellow crystals from  $\text{HCO}_2\text{H}$  and  $\text{H}_2\text{O}$  mixt. A was reduced with  $\text{Hg}\cdot\text{Na}$  to  $\text{O}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}$  and this lactone with  $\text{NH}_2\text{NH}_2\cdot\text{H}_2\text{O}$  gave *butyrolactone hydrazone*,  $\text{H}_2\text{NNHC}(\text{OH})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}$ , leaves from  $\text{AcOEt}$ , m.  $93^\circ$ . The

calcium salt of A was prepd. and the phenylhydrazone. A with  $\text{H}_2\text{SO}_4$  polymerizes to

the trimer  $\text{HO}_2\text{C}(\text{CH}_2)_2\text{CH}$    $\text{CH}(\text{CH}_2)_2\text{CO}_2\text{H}$ , m. 167, slightly sol. in  $\text{Et}_2\text{O}$ ,

$\text{AcOEt}$ , and in  $\text{Na}_2\text{CO}_3$  but the aldehydic properties are masked—there is no coloration with the Schiff reagent, no semicarbazone, *p*-nitrophenylhydrazone, nor oxime could be formed, and the product did not reduce  $\text{NH}_2\cdot\text{AgNO}_3$ . The bonds forming the cycle are attached to the O atoms. References to this compd. are given. The dimer m.  $147^\circ$  (C. A. 6, 1749). The trimer when distd. gave A and *hydroxybutyrolactone oxide*,  $(\text{O}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}\text{---})_2\text{O}$ . A can exist as *hydroxybutyrolactone*. Elimination of  $\text{H}_2\text{O}$

from this compd. would lead to the oxide. The oxide when treated with semicarbazide gave the semicarbazone of A and when treated with alc.-HCl,  $\text{OHCCH}\cdot\text{CHCO}_2\text{Et}$  was formed. With NaOH the Na salt of A is formed and when the latter is acidified aldolization results in the formation of *butyrolactone aldehyde succinic acid*,  $\text{O}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}$

$\text{CH}(\text{CHO})\text{CH}_2\text{CO}_2\text{H}$ , which yields a semicarbazone, white powder, slightly sol. in alc., m.  $225^\circ$ .  $\text{SOCl}_2$  or  $\text{PCl}_5$  when acting on A as the trimer gave *chlorobutyrolactone*,  $b_{18}$   $101^\circ$ , which when distd. loses HCl and when treated with abs. alc. gave *ethyl acetal-succinate*,  $\text{EtO}_2\text{CCH}_2\text{CH}_2\text{CH}(\text{OEt})_2$ . C. discusses the relation between B, itaconic acid, F and A and he reproduces the work of Swarts (Bull. acad. roy. Belg. [2] 33, 1873).

$\text{CH}_3\text{BrCBr}(\text{CO}_2\text{H})\text{CH}_2\text{CO}_2\text{H}$  (AA) was heated at  $180^\circ$  and bromoitaconic acid, m.  $190-5^\circ$ , was prepd. This on treatment with  $\text{H}_2\text{O}$  gave B, m.  $170^\circ$ . AA when heated with  $\text{H}_2\text{O}$  gave B. C. concluded that considering the monohalogenated acids prepd. by Wislicenus, Boklen and Reuthe and by Swarts, the true mono-Cl deriv. was obtained by the former experimenters among the products of the action of  $\text{PCl}_5$  on F. C. believes that Swarts' product is  $\text{CH}_3\text{CH}_2\text{OCH}(\text{CBrCO}_2\text{H})$  and that Frankenstein's hydroxy-

itaconic acid (Diss. p. 22-31) is formylsuccinic acid (DD) in the enolic form,  $\text{HOCH}_2\text{C}(\text{CO}_2\text{H})\text{CH}_2\text{CO}_2\text{H}$ . CC treated in abs. alc. with KOH gave after elimination of alc. and treatment with HCl, *N*-1-carbamyl-4-acetyl-5-pyrazolone,  $\text{HO}_2\text{CCH}_2\text{CH}(\text{CH}:\text{N.N}(\text{CONH}_2)\text{CO})$  (EE), crystals, m.  $185^\circ$ , which result from the loss of a mole

of  $\text{H}_2\text{O}$  from the semicarbazone of DD. To throw light on the course of the reaction taking place when CC is hydrolyzed, C. sapond.  $\text{MeC}:\text{N.NH.CO.NH.CH}_2\text{CO}_2\text{Et}$  and

prepd. by this means *N*-1-carbamyl-3-methyl-5-pyrazolone, m.  $170^\circ$ , which with  $\text{FeCl}_3$  gave a violet coloration (Compt. rend. 132, 975(1901)). A was esterified in alc. with HCl during 40 hrs., yielding ethyl aldehydosuccinate (FF),  $b_{11}$   $84-5^\circ$ , and also the acetal,  $b_{11}$   $101-2^\circ$ . Twenty-five g. A gave 16.4 g. of the acetal and 5.6 g. of the ester. When A as the trimer was esterified only the ester was obtained. FF yielded a semicarbazone, brilliant needles, m.  $135^\circ$ , from alc.; the *p*-nitrophenylhydrazone, red-brown crystals, m.  $80-1^\circ$ , from alc.; the oxime,  $b_{14}$   $139^\circ$ , and ethyl naphthochinchominypropionate, yellow leaflets, m.  $268^\circ$ . FF with  $\text{NH}_2\text{NH}_2$  gave 6-pyridazinone, m.  $37^\circ$ ,  $b_{11}$   $143^\circ$ , sol. in  $\text{Et}_2\text{O}$ ,  $\text{C}_6\text{H}_6$ , alc. and  $\text{AcOEt}$ . FF with  $\text{MgEtBr}$  gave 3-ethyl-3,6-octanediol (GG),  $b_{20}$   $148^\circ$ , m.  $41^\circ$ , from petr. ether. GG treated with  $\text{Ac}_2\text{O}$  gave 3-ethyl-3,6-octanediol 6-ethanoate (HH),  $b_{18}$   $146-7^\circ$ ,  $\text{Et}_2\text{C}(\text{OH})\text{CH}_2\text{CH}_2\text{CH}(\text{OAc})$ . GG when treated with  $\text{H}_2\text{SO}_4$  gave 3-ethyl-3,6-octanediol oxide (II),  $b_{18}$   $68-9^\circ$ . This compd. has an odor of camphor. II with  $\text{MgEtBr}$  did not give a gaseous product but HH did and therefore HH contains an alc. group. 3-Ethyl-3,6-octanediol 3,6-diphenylurethan, white powder, m.  $121^\circ$ , was formed when GG was treated with  $\text{PhNCO}$  during 2 months. Two moles  $\text{CH}_2(\text{CO}_2\text{Et})_2$  were condensed with FF in the presence of  $\text{Et}_2\text{NH}$  (Knovenagel) and the product of the condensation was sapond. 6 hrs. with HCl and the resulting acid was esterified with  $\text{H}_2\text{SO}_4$  and alc. Diethyl 3-ethyl-ethanoate-1,6-hexanedioate,  $\text{EtO}_2\text{CCH}_2\text{CH}_2\text{CH}(\text{CH}_2\text{CO}_2\text{Et})\text{CH}_2\text{CO}_2\text{Et}$  (JJ),  $b_{18}$   $200^\circ$ . JJ when treated with KOH and then with HCl gave the corresponding triacid (KK), white powder, m.  $122^\circ$ . The anhydride was formed when the triacid was refluxed with  $\text{AcCl}$ , white cryst. powder, m.  $133^\circ$ , insol. in  $\text{C}_6\text{H}_6$ ,  $\text{C}_7\text{H}_8$ , petr. ether. The monoanilide of KK, a white powder from alc. m.  $151^\circ$ . The mono-*p*-toluidide, m.  $207^\circ$ , white powder. Adipic acid,  $\text{HO}_2\text{C}(\text{CH}_2)_4\text{CH}:\text{CHCO}_2\text{H}$ , was formed when A was allowed to stand 4 days with  $\text{C}_6\text{H}_5\text{N}$  and  $\text{CH}_2(\text{CO}_2\text{H})_2$ , white powder, m.  $208-10^\circ$ . It decolorizes  $\text{KMnO}_4$  and absorbs Br. LL when treated with  $\text{MgEtBr}$  at  $0^\circ$  for 1 hr. gave  $\alpha,\alpha$ -diethyl- $\alpha'$ -ethoxyletrahydrofurfuran,  $b_{11}$   $69^\circ$ . It has no action on Schiff's reagent, contains no ethylenic linkage, shown by the use of alk.  $\text{KMnO}_4$ , and it does not react in the cold with KOH. A second product of the action of  $\text{EtMgBr}$  was 3,6-diethyl-3,6-octanediol, m.  $69^\circ$ ,  $b_{11}$   $154^\circ$  (Compt. rend. 132, 833) (MM). The phenylurethan m.  $187-8^\circ$ , from  $\text{C}_6\text{H}_5$ . MM was prepd. synthetically by treating  $\text{EtMgBr}$  with  $\text{EtBr}$ . MM came from  $(\text{CH}_2\text{CO}_2\text{Et})_2$  as an impurity in LL. MM yielded with  $\text{H}_2\text{SO}_4$  3,6-diethyl-3,6-octanediol oxide,  $b_{14}$   $95-6^\circ$ . 3-Ethyl-3,6-hexanediol (NN),  $b_{21}$   $144-5^\circ$ , was prepd. by the action of  $\text{EtMgBr}$  on butyrolactone formed by the action of KOH on  $\text{EtO}_2\text{CCH}_2\text{CH}_2\text{CH}_2\text{Cl}$ . NN in  $\text{Ac}_2\text{O}$  when warmed 2 hrs. on the steam bath gave 3-ethyl-3,6-hexanediol 6-ethanoate,  $\text{Et}_2\text{C}(\text{OH})\text{CH}_2\text{CH}_2\text{CH}_2\text{OAc}$ . A diethanoate could not be formed, probably because of

steric hindrance. The *diphenylurethan* of NN m. 106°, from alc. and from  $C_6H_5$ . Ethylsuccinic acid aldehyde (OO),  $OHCCH_2CETHCOC_2H_5$ , was prepd. by hydrolyzing  $OHCCH(CO_2Et)CHETCO_2Et$  with  $(CO_2H)_2$  (yield 60%); it decomp.  $KHCO_3$ , reduces  $NH_4AgNO_3$ , Fehling soln. and acts on Schiff's reagent. The *semicarbazone* m. 156°, from alc.; the *p-nitrophenylhydrazone* m. 164°, from AcOH; the *oxime* m. 70°, from  $C_6H_6$  with petr. ether; *naphthocinchoninyl- $\alpha$ -ethylpropionic acid*, yellow crystals infusible at 280°; the *phenylhydrazide phenylhydrazone*, white crystals, m. 175°. OO does not polymerize when esterified with HCl in alc.; the *ester* obtained,  $b_p$  103–4°, reacts with Schiff's reagent,  $NH_4AgNO_3$ , and Fehling soln. It gave a *semicarbazone* and *p-nitrophenylhydrazone*. A second product from the esterification was *ethoxylethylbutyrolactone*,  $EtCH.CH_2CH(OR).O.CO$ ,  $b_{25}$  114–5°, an isomer of the ester. The

introduction of an Et group into A prevents the polymerization of OO and the acetal is not formed. The results agree with those of Blaise and Courtot (*Bull. soc. chim.* **35**, 989) on acid aldehydes.

H. E. W.

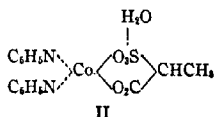
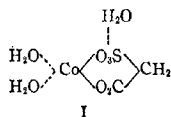
**Residual affinity and coördination. VIII. Interaction of tellurium tetrachloride and  $\beta$ -diketones.** GILBERT T. MORGAN, HARRY DUGALD, K. DREW AND E. A. COOPER. *J. Chem. Soc.* **121**, 922–40(1922); cf. *C. A.* **16**, 1366. The initial reaction product between  $TeCl_4$  and  $AcCH_2COMe$  is  $AcCH_2COCH_2TeCl_3$ , which, in EtOH-free  $CHCl_3$ , condenses with a 2nd mol. of  $AcCH_2COMe$  to form *tellurium bisacetylacetonate dichloride*, silvery flakes, m. 115°. In  $CHCl_3$   $FeCl_3$  gives a blood-red color. *Tellurium bisbenzoylacetonate dichloride*, flattened yellowish white needles, m. 148°. *Tellurium 3-methylacetylacetonate* (A), by the action of  $KHSO_4$  on the di-Cl deriv., small hexagonal pale golden-yellow plates, decomp. 170°, and subliming in vacuum at 140° to small compact yellow prisms. It is non-enolic towards Fe and Cu salts and is comparatively insol. in cold 5 N NaOH. The *dichloride* is obtained from  $TeCl_4$  and  $AcCHMeCOMe$  in EtOH-free  $CHCl_3$ , and forms stout hexagonal needles or prisms with obliquely truncated ends, decomp. about 190°. The *dibromide* results by the addition of Br to A, pale yellow prisms, decomp. 152–3°. The *diiodide* forms reddish purple crystals, sintering 131–4° and decomp. 169–71°. *Tellurium 3-ethylacetylacetonate*, yellow needles or compact prisms from EtOH or lustrous primrose-yellow hexagonal leaflets from  $C_6H_6$ , subliming slowly in vacuum at 130° in long needles, changing at 140° to small yellow prismatic crystals, m. 142°, and giving Te at 160°,  $a:b:c = 1:1:0.7221$ ,  $q(011)$ ,  $r(101)$ ,  $m(110)$ ; Fedorov complex symbol,  $4o(45^\circ 36') \pm 0$ . *Dichloride*, lustrous, hexagonal prisms, blackening 185–90°. Prolonged boiling with HCl caused decompn. into  $TeCl_4$  and  $C_6H_5O_2Et$ . The dust has an extremely irritating action on the mucous membrane of the nose. *Dibromide*, lustrous, pale yellow crystals, intumescing 161–70°. *Diiodide*, light scarlet, decomp. 176°. *Tellurium chloroacetylacetonate*, pale golden yellow needles, decomp. 153–4°. It is sol. in aq.  $Na_2CO_3$  and in NaOH, the latter soln. being unstable and liberating Te. *Dichloride*, obtained in small yield on condensing  $TeCl_4$  and  $AcCHClCOMe$  in ordinary dried  $CHCl_3$ , decomp. 161–2°. The main product of the reaction is *tellurium bischloroacetylacetonate dichloride*, transparent, feathery, prismatic needles, decomp. 131–2°. It gives a red color with  $FeCl_3$  and is decompd. by  $KHSO_4$  to Te and  $AcCHClCOMe$ . *Tellurium O-ethylpivalylacetonate trichloride*, transparent yellowish white needles, sinters 114°, m. 116°. It is non-phenolic towards  $FeCl_3$ , and is decompd. by cold NaOH. If pure  $CHCl_3$  is used, *tellurium bispivalylacetonate dichloride* is obtained as glistening flakes, decomp. 133°. It reacts with  $Cu(OAc)_2$  and gives a red color with  $FeCl_3$ .  $Bz_2CH_2$  and  $TeCl_4$  in pure  $CHCl_3$  gave *tellurium dibenzoylmethane trichloride*, golden yellow and very unstable, decomp. in the air to  $Bz_2CH_2$  and  $TeOCl_2$ . These derivs. are not true germicides but powerful growth inhibitors for *Bacillus coli*. The propionyl deriv. (to be described) exerts a definite inhibitory effect in as low a concn. as 1 in 5,000,000.

C. J. Wess



The action of thionyl chloride on the  $\alpha$ -hydroxy acids. E. E. BLAISE AND M. M. MONTAGNE. *Compt. rend.* 174, 1173-4 (1922).—Two compounds,  $\text{ClSOOCH}_2\text{COCl}$  (A),  $b_p$  78–82°, and  $\text{CH}_2\text{ClCOOCH}_2\text{COCl}$  (B),  $b_p$  99–101°, are obtained by the action of  $\text{SOCl}_2$  on  $\text{CH}_2(\text{OH})\text{CO}_2\text{H}$ . A heated at 180° gives  $\text{SO}_2$  and  $\text{ClCH}_2\text{COCl}$ . With  $\text{H}_2\text{OHCl}$ ,  $\text{H}_2\text{SO}_4$ , and  $\text{CH}_2(\text{OH})\text{CO}_2\text{H}$  result. MeOH gives  $\text{CH}_2(\text{OH})\text{CO}_2\text{Me}$ ,  $b_p$  63°, and in  $\text{Et}_2\text{O}$ ,  $\text{PhNH}_2$  gives  $\text{SO}(\text{OCH}_2\text{CONHPh})_2$  (C),  $m.$  140°, decomp. by  $\text{H}_2\text{O}$ , slightly sol. in cold EtOH, very sol. in hot EtOH. C is stable to heat in dry air but loses  $\text{SO}_2$  on heating in moist air. C is also obtained by treating A with  $\text{CH}_2(\text{OH})\text{CONHPh}$ . B may also be obtained by heating  $\text{ClCH}_2\text{COCl}$  with  $\text{CH}_2(\text{OH})\text{CO}_2\text{H}$  and heating the product with  $\text{SOCl}_2$ . B gives an anilide, platelets,  $m.$  119°. T. E. DUNLAP

The formation of salts of sulfocarboxylic acids. I. The cobaltous and cupric salts of sulfacetate and  $\alpha$ -sulfopropionic acids. H. J. BACKER AND J. V. DUBSKY. *Rec. trav. chim.* 41, 145-51 (1922).—The simple and complex Co and Cu salts of sulfacetate (A) and  $\alpha$ -sulfopropionic acids were of interest because of their 2 different acid functions. Cobalt sulfacetate (I) was prepd. from the Ba salt and  $\text{CoSO}_4$ . With  $\text{C}_5\text{H}_5\text{N}$  it gives a complex in which 2  $\text{H}_2\text{O}$  mols. are substituted with 2  $\text{C}_5\text{H}_5\text{N}$  mols. In both of



these complexes 1  $\text{H}_2\text{O}$  mol. is probably bound to a  $\text{SO}_3$  group. I treated with an equimol. amt. of A gives cobalt acid sulfacetate (C),  $[\text{Co}(\text{H}_2\text{O})_4] [\text{O}_2\text{S.CH}_2\text{CO}_2\text{H}]_2$  as pale orange crystals, which lose all their  $\text{H}_2\text{O}$  at 105°. The corresponding acid sulfate of Co is unknown, and could not be prepd. C treated with  $\text{CoCO}_3$  gave I. Cobalt  $\alpha$ -sulfopropionate was obtained only as a sirup, which with  $\text{C}_5\text{H}_5\text{N}$  gave II, corresponding to the similar deriv. of I. Cobalt acid  $\alpha$ -sulfopropionate,  $[\text{Co}(\text{H}_2\text{O})_4] [\text{O}_2\text{SCHMeCO}_2\text{H}]_2$

loses 4  $\text{H}_2\text{O}$  at 105°. Neutral copper sulfacetate (D),  $\text{Cu} \begin{array}{c} \diagup \text{O}_2\text{S} \diagdown \\ \diagdown \text{O}_2\text{C} \diagup \end{array} \text{CH}_2$ , seps. as a bright blue-green cryst. powder, containing 1 mol.  $\text{H}_2\text{O}$  firmly fixed; it unites with  $\text{C}_5\text{H}_5\text{N}$ , giving the pyridine complex (E)  $\text{C}_5\text{H}_5\text{N} \cdots \text{Cu} \begin{array}{c} \diagup \text{O}_2\text{S} \diagdown \\ \diagdown \text{O}_2\text{C} \diagup \end{array} \text{CH}_2$ , as deep blue crystals.

Attempts to prep. the polymer of C by treating it or the free acid with  $\text{CuO}$  gave C, identical with that obtained above from the Ba salt and  $\text{CuSO}_4$ . When 0.5 mol. of  $\text{CuO}$  is dissolved in A a little  $\text{CuO}$  is reduced but the soln. on filtering and evapg. gave acid copper sulfacetate (F),  $[\text{Cu}(\text{H}_2\text{O})_4] [\text{O}_2\text{S.CH}_2\text{CO}_2\text{H}]_2$ , as bluish green crystals that lose

4  $\text{H}_2\text{O}$  at 95° and the 5th at 105° (with decompn.). On adding  $\text{C}_5\text{H}_5\text{N}$  to the soln. E sepd. and pyridine sulfacetate remained in the soln. Copper  $\alpha$ -sulfopropionate (G),  $\text{H}_2\text{O} \cdots \text{Cu} \begin{array}{c} \diagup \text{O}_2\text{S} \diagdown \\ \diagdown \text{O}_2\text{C} \diagup \end{array} \text{CHCH}_3$ , was obtained from the Ba salt and  $\text{CuSO}_4$  and seps. with 3 mols. of  $\text{H}_2\text{O}$ . In the corresponding  $\text{C}_5\text{H}_5\text{N}$  salt 2  $\text{H}_2\text{O}$  mols. are replaced with  $\text{C}_5\text{H}_5\text{N}$ . The acid copper  $\alpha$ -sulfopropionate is analogous to F. The salts of these 2

acids are closely analogous. The  $H_2O$  remaining in the  $C_6H_5N$  complex is less firmly bound than in the corresponding  $H_2O$  compd. It is supposed that the metal having been rendered more positive by the presence of  $C_6H_5N$  utilizes the affinity of the  $SO_3H$  group more fully.

E. J. WITZEMANN

**Preparation of ethyl carbamate.** L. GUERCI. *Giorn. chim. ind. applicata* **4**, 60(1921).—Urea nitrate is treated with abs. EtOH in presence of  $NaNO_3$ . The app. consists of a 10-l. flask connected in series with a good reflux condenser, a  $CaCl_2$  tube and a wash bottle contg. Hg, the latter to maintain a pressure of about 0.5 atm. The method is as follows: Place about 3 kg. abs. EtOH and 1 kg. urea nitrate in the flask. Heat to 60–70°. Add  $NaNO_3$  in portions of 25 g. at such a rate as to complete a total addn. of 561 g. in 2 hrs. Allow to react for another hr. Distil the EtOH rapidly at reduced pressure. There remains an oily mass solidifying on cooling. Ext. 3 times with 500 cc. hot  $C_6H_6$ , dist. off the solvent almost completely. On cooling the urethan crysts. in beautiful white needles, m. 47–50°, recryst. from  $C_6H_6$  in large, long, colorless, shining tablets, which m. 49–50° when well dried. The yield is 80%. The  $NaNO_3$  and urea nitrate must be well dried.

ROBERT S. POSMONTIR

**Action of amines on semicarbazones. I. Preparation of an optically active semicarbazide.** F. J. WILSON, I. V. HOPPER AND A. B. CRAWFORD. *J. Chem. Soc.* **121**, 866–70(1922).—Acetone  $\delta$ -benzylsemicarbazone, long, colorless prisms, m. 113°, results by condensing  $Me_2C:NNHCONH_2$  and  $PhCH_2NH_2$  at 180°, and yields  $\delta$ -benzylsemicarbazide hydrochloride upon heating at 50° with 12 parts  $N$  HCl until soln. results, felted mass of needles, m. 224–5°; with EtONa, the free semicarbazide is obtained, small, needle-shaped crystals, m. 111°; benzylidene derivative, from the HCl salt and  $BzI$ , large, lustrous prisms, m. 139°. *dl*-Acetone  $\delta,\alpha$ -phenylethylsemicarbazone, prisms, m. 114°. Active compound, by using a base with  $[\alpha]_D^{25}$  40.8°, rhombic prisms, m. 84°,  $[\alpha]_D^{25}$  –67.3°. *dl*- $\delta,\alpha$ -Phenylethylsemicarbazide hydrochloride, small prisms, m. 165° (decompn.). Active compound, pearly plates, m. 180° (decompn.),  $[\alpha]_D^{25}$  66°.

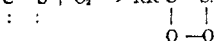
C. J. WEST

**Reactions of thiosemicarbazones. I. Action of halogen compounds.** F. J. WILSON AND ROBERT BURNS. *J. Chem. Soc.* **121**, 870–6(1922).—Acetone thiosemicarbazone sodium derivative (A),  $C_6H_5N_2SNa$ , white powder, sol. in alc. and  $H_2O$ . EtI decompd. A, with evolution of EtHS.  $PhCH_2Cl$  and A gave acetone  $S$ -benzylthiosemicarbazone (B), long needles, m. 51–2°, decompd. by boiling with 2  $N$  NaOH into  $NH_3$ ,  $Me_2CO$  and  $PhCH_2SH$ . Treatment with  $PhSO_2Cl$  and EtONa gave the sodium derivative of a sulfonamide,  $Me_2C:NN:C(SCH_2Ph)NNaSO_2Ph$ , white powder, very sol. in  $H_2O$ . With  $N$  HCl, B gives  $S$ -benzylthiosemicarbazide hydrochloride, white, granular ppt., m. 124–6° (decompn.). Sulfate, small needles, m. 148° (slight decompn.). Benzaldehyde derivative, needles, m. 190°. The action of *l*-menthyl chloroacetate or of  $CICH_2CO_2Et$  upon A gave a new type of  $\psi$ -thiohydantoin derivative,  $Me_2C:NN:C.NH.CO.CH_2S$ ,

plates, m. 175–6°. The constitution was established by hydrolysis with concd. HCl,  $Me_2CO$  and 2,4-diketotetrahydrothiazole being formed. The action of  $CICO_2Et$  upon A in  $C_6H_6$  gave a product,  $C_6H_5N_2S$ , lustrous flakes, m. 188–9°. In alc.  $Me_2C:NN:CS-NH_2$  is regenerated.

C. J. WEST

**The autoxidation of organic sulfur compounds.** MARCEL DELEPINE. *Compt. rend.* **174**, 1291–3(1922).—A considerable no. of org. compds. containing doubly bound S are oxidized by the air at ordinary temps., giving fumes and light visible in a dark room (cf. C. A. **4**, 2934; **5**, 3411; **6**, 1749, 2421). An "ozonide" containing S may be formed:  $RR'C:S \rightarrow RR'C-S + O_2 \rightarrow RR'C-S$ . The ozonide decomp. into



$RR'CO + SO$ , the latter being oxidized in turn (cf. *Bull. soc. pharmacol.* **17**, 501(1910)).

This autoxidation is remarkable in that it affects only a minute proportion of the amt. of vapor present (shown by detns. of  $\text{SO}_2$  and  $\text{SO}_3$ ), even in the presence of a large excess of air, and then ceases immediately, and permanently if the reaction mixt. be sealed. The presence of fixed alkalis and of  $\text{NH}_4\text{OH}$  with, resp., sulfo-carbamic esters and the majority of other S compds. ( $\text{SC}(\text{OR})\text{OR}'$ ,  $\text{SC}(\text{OR})_2$ ,  $\text{SCClOMe}$ ,  $\text{SCCl}_2$ ) strongly promotes the completion of the oxidation (cf. *C. A.* 4, 2806; 12, 2547). Oxyluminescence is produced in  $\text{CSCl}_2$  or  $\text{MeCSOMe}$  with 5 mm. pressure of O; in  $\text{CS}(\text{OMe})\text{SMe}$  with 7 mm.; and in  $\text{Me}_2\text{NCSOMe}$  with 25 mm.; the presence of  $\text{H}_2\text{O}$  seems unnecessary. A mixt. of vapor and air which has glowed and produced fumes shows the same phenomena repeatedly when exposed to successive portions of fresh air. The very small amt. of vapor oxidized each time may be reduced even to zero by the presence of substances such as  $\text{Et}_2\text{O}$ ,  $\text{AcH}$ , turpentine, petr. ether,  $\text{Me}_2\text{CO}$ , pyridine,  $\text{CS}_2$ ,  $\text{SO}_2$ , or  $\text{H}_2\text{S}$ ; the phenomena of light and fumes are prevented by widely different amts. of these anti-catalysts; but  $\text{CSCl}_2$  explodes with  $\text{Et}_2\text{O}$  vapor. The activity of such mixts. is restored by the introduction of  $\text{NH}_4\text{OH}$ , unless the proportion of anti-catalyst is large. The lower satd. aliphatic acids promote autoxidation. The reaction, characterized by the extremely small amt. of substance oxidized, is favored if the concn. of vapor is between certain limits, as in the case of explosive mixts. of gases; if too high, oxidation is indefinitely arrested: the S compds. act as their own anti-catalyst.

A. R. ALBRIGHT

**Some guanidonium salts.** W. MARCKWALD AND F. STRUWE. *Ber.* 55B, 457-63 (1922).—It was shown in 1915 (cf. Ger. pats. 309,297, 309,298) that the chlorates and perchlorates of certain bases of the urea group, especially guanidonium, are very effective explosives. *Guanidonium chlorate*,  $\text{CH}_3\text{N}_3\text{HClO}_3$ , from the sulfate and  $\text{Ba}(\text{ClO}_4)_2$ , m. 98-100°, is, for a chlorate, relatively little sensitive to shock, is about like picric acid in explosive effectiveness but is not as suitable for an explosive because it is not sufficiently stable on storage. In this respect it is surpassed by the *perchlorate*, which is about equal to it in sensitiveness to shock and explosive power; it may be prepd. by double decompn. or by fusing together equiv. amts. of dicyanodiamide and  $\text{NH}_4\text{ClO}_4$  at 160°; it dissolves at 0° in about 8, at 50° in 1 part  $\text{H}_2\text{O}$  and m. about 250°; treated in alc. with 1 mol. KOH, filtered from the  $\text{KClO}_4$ , concd. *in vacuo* at 30-5° and allowed to stand for weeks *in vacuo* over  $\text{P}_2\text{O}_5$  it yields a mass of deliquescent crystals containing 93-99.5% free guanidine (A), m. about 50°, solidifies over a free flame with formation of melamine, can be sharply titrated both with Me orange and with phenolphthalein. The strong alkalinity of its aq. solns. shows that it is present chiefly as the hydroxide (B); such solns. behave towards those of metal salts like the fixed alkalis, the ppts. of the hydroxides of Al, Cr, Pb and Sn redissolving in an excess of the B. In accordance with its strong basicity, it forms stable salts with very weak acids. *Guanidonium thio-sulfate*, from the perchlorate in alc. with  $\text{K}_2\text{S}_2\text{O}_8$  in  $\text{H}_2\text{O}$ , contains 1  $\text{H}_2\text{O}$ ; *sulfite*, from A in alc. with  $\text{SO}_2$ ; *hydrosulphide*, similarly obtained, yellowish leaflets with 0.5  $\text{H}_2\text{O}$ ; *xanthate*, faintly yellow crystals, m. 113°; *borate*,  $(\text{CH}_2\text{N}_3)_2\text{B}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$ ; *silannate*, long crystals with 3  $\text{H}_2\text{O}$ , hydrolyzed by hot  $\text{H}_2\text{O}$ ; *melasilicate*,  $(\text{CH}_2\text{N}_3)_2\text{SiO}_3 \cdot x\text{H}_2\text{O}$ , sometimes seps. in long spears, at other times gelatinizes, and the  $\text{H}_2\text{O}$  content varies greatly, in one case being over 70%; *formate*, obtained in cryst. form from the perchlorate and  $\text{HCO}_2\text{K}$ , m. 70-5°; *nitromethane*,  $\text{CH}_3\text{N}_3 \cdot \text{MeNO}_2$ , from A and 1 mol.  $\text{MeNO}_2$  with a little abs. alc., needles quickly becoming yellow on clay, cannot be titrated directly with Me orange but can be titrated by treating with excess of HCl and titrating back with  $\text{Ba}(\text{OH})_2$ ; *phenolate*, m. 67°; *p-cresolate*, m. 147-50°; *benzenesulfonamide*, scales, m. 188° (decompn.); *phthalimide*, m. 176-9° (decompn.).

C. A. R.

**The saponification of the mono- and diethyl esters of diethylmalonic acid.** PHILIPPE DUMESNIL. *Bull. soc. chim.* 31, 320-4 (1922).—The attempt was made to effect sapon. of  $\text{Et}_2\text{C}(\text{CO}_2\text{Et})_2$  (A) more readily (cf. *C. A.* 16, 58) by changing the conditions.

A was let stand 95 hrs. at 15° in 75% EtOH with 1.25 times the theoretical NaOH. At the end of 95 hrs. only 8.8% of  $\text{Et}_2\text{C}(\text{CO}_2\text{Na})_2$  was formed, the remainder being  $\text{Et}_2\text{C}(\text{CO}_2\text{Na})\text{CO}_2\text{Et}$ . The mean value of  $k$  was  $4.26 \times 10^{-4}$ . Boiling A in 50% EtOH with twice the theoretical NaOH gave a mean value of  $k$  of  $1380 \times 10^{-4}$ . The sapon. was 90.5 and 95.11% complete as detd. by titration and by extn., resp. Boiling  $\text{Et}_2\text{C}(\text{CO}_2\text{Et})\text{CO}_2\text{H}$  with dil. EtOH and 2.5 times the theoretical NaOH gave a mean  $k$  value of  $120 \times 10^{-4}$ . The sapon. was 47.5 and 52% complete by titration and by extn. The ratio  $k'/k$  was thus 0.087, a similar value to that for Et succinate (cf. Knoblauch, *Z. physik. Chem.* 26, 96(1898)) in spite of the great difference in the individual  $k'$  and  $k$  values.

C. C. DAVIS

**Esterification of monoethyl diethylmalonate and of diethylmalonic acid.** PHILIPPE DUMESNIL. *Bull. soc. chim.* 31, 419-20(1922).—Esterification of the acid ester of  $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$  to the neutral ester is much more difficult than esterification of the free acid to the acid ester. After refluxing a soln. of 18.8 g. of the acid ester in 100 cc. abs. EtOH contg. 2.5% HCl for 90 hrs. the product consisted of 7.6 g. of unchanged acid ester and 10.5 g. of a mixt. of the neutral ester with about 10% of EtOAc. On the other hand, 15 hrs. refluxing of 16 g. of  $\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$  with 100 cc. abs. EtOH contg. 2.5% HCl gave 13.5 g. of the acid ester, 2.4 g. of the neutral ester, 0.9 g. of unchanged acid and only traces of EtOAc.

A. W. DOX

**Quinhydrone of the maleic acid anhydride series.** PAUL PFEIFFER (with E. FLATER). *Ber.* 55B, 413-29(1922); cf. *C. A.* 13, 1471.—It was shown in the earlier paper that anhydrides of the type of maleic anhydride (A) yield characteristic quinhydrone-like compds., A and related compds. giving with numerous aromatic substances (hydrocarbons, phenols, amines, etc.) more or less deeply colored solns. whose colors obey the rules followed by the quinhydrone; some of the addition products present in these soln. were isolated in solid cryst. form. It became of importance to det. exactly how far the type A could be changed without destroying its ability to form these quinhydrone-like compds. and also to isolate a larger no. of them in order to be able to characterize this new type of substances well. As regards the first point it had already been

shown that while citraconic anhydride (B), which contains the grouping  $-\text{C}(\text{:O})\text{C}:\text{C}(\text{:O})-$  (also present in quinone), dissolves in  $\text{PhNMe}_2$  with orange color, the isomeric itaconic anhydride (C) at first gives no such color reaction; the subsequent appearance of the yellow color is due to the C rearranging into B, a reaction greatly accelerated by  $\text{PhNMe}_2$ . Equally sharp is the difference in behavior of B and C towards  $\text{PhOH}$  and  $o\text{-MeC}_6\text{H}_4\text{OMe}$ . Whether the above grouping forms part of a ring, as in quinone or A, or of an open chain ( $\text{PhCOCH}:\text{CHCOPh}$ , di-Me fumarate, di-Me tetrachlorophthalate) seems to be of no material importance. In agreement with these views is the behavior of  $o\text{-C}_6\text{H}_4(\text{CHO})_2$ , which dissolves in  $\text{PhNMe}_2$  with orange-yellow color, while the isomeric phthalide dissolves without the least color. Similarly,  $o\text{-C}_6\text{H}_4(\text{COCl})_2$  gives with guaiacol and acenaphthene (to which a little xylene has been added to lower the m. p.) greenish yellow solns. while the asym. chloride forms colorless solns. In the second part of the problem, viz., the isolation of the addition products, no success was had with A itself and its Me and halogen derivs. but tetrachloro- and tetrabromophthalic anhydrides yielded such products with the most varied aromatic hydrocarbons, phenols, phenol ethers and amines, halogenation of the  $\text{C}_6\text{H}_4(\text{CO})_2\text{O}$  having an influence upon its additive power similar to that of the halogenation of quinone; judging from the color, however, addition products of the non-halogenated compds. also exist in melts and solns. Tetrachlorophthalimide likewise forms colored addition products. The following *tetrachlorophthalic anhydride addition products* were prepd.; *mesitylene*, light yellow needles weathering in the air at room temp.; *naphthalene*, from the components in hot AcOH allowed to cool slowly, greenish yellow silky needles weathering on heating;  *$\alpha$ -methylnaphthalene*,

greenish yellow needles weathering on heating; *acenaphthene*, fine, golden yellow needles from AcOH, m. 237–40°, stable in the air; *anthracene*, golden yellow needles from AcOH, m. 195°, stable in the air; *phenanthrene*, long, yellow needles from AcOH, m. 190°; *α-bromonaphthalene*, light yellow needles with faint silky luster, stable in the air but decompd. into its components on gentle heating, seps. from PhBr in leafy needles; *α-naphthol*, yellow-orange needles from AcOH, m. 250°, stable in the air; *β-naphthol*, yellow needles from AcOH, m. 210°; *α-naphthyl ethyl ether*, flat deep yellow needles easily weathering on heating; *β-methyl ether*, greenish yellow needles from AcOH, weather on heating; *biphenylene oxide*, long, greenish yellow needles from AcOH; *carbazole*, yellow needles from AcOH, m. 210°. *3,6-Dichlorophthalic anhydride-acenaphthene*, lemon-yellow needles from AcOH, m. 119–20°. *Tetrachlorophthalimide-α-naphthyl methyl ether*, lemon-yellow needles; *ethyl ether*, lemon-yellow needles, losing the  $C_{12}H_{10}Br$  completely on gentle heating. *Tetrabromophthalic anhydride addition products: naphthalene*, light green-yellow needles from AcOH, lose their  $C_{10}H_8$  quant. at 100°; *acenaphthene*, long, deep yellow needles losing the  $C_{12}H_{10}$  at 100–20°; *α-naphthyl ethyl ether*, deep yellow needles. *Chloranil-acenaphthene*, long, deep black needles from AcOH; rubs to a blue-violet powder, change, at 120° to S-yellow with loss of the  $C_{12}H_{10}$  but without change in the cryst. form.

C. A. R.

**New syntheses of pyrimidines.** E. CHERBULIEZ AND K. N. STAVRITCH. *Helvetica Chim. Acta* 5, 267–84 (1922).—Upon treating methyleneasparagine (A) with NaOBr it was found that, instead of a deriv. of diaminopropionic acid as expected according to the Hofmann reaction, the product was *6-hydroxy-5-bromopyrimidine-4-carboxylic acid* (B), the constitution being ascertained by conversion to *6-hydroxypyrimidine* (C) which is known. In effecting this condensation to the pyrimidine deriv. NaOBr has both an oxidizing and a brominating action.  $KMnO_4$  gave a similar condensation with A, forming *6-hydroxypyrimidine-4-carboxylic acid* (D), which on distn. gave C readily. C. and S. have studied these reactions and the resulting derivs. of methylene-, ethylidene-, and benzylideneasparagine. **I. Oxidation with NaOBr.** This reaction goes best with a large excess of NaOH at temps. below –4°. Thus 9 g. A in 62.5 cc. N NaOH are treated with 30 g. Br in 125 cc. 5 N NaOH, at a temp. below –4°. This takes 45 min. After 1 hr. more the soln. is acidified with HCl and B slowly crystals. Yield 11.6 g. (78%), colorless needles, m. 206–7° with evolution of  $CO_2$ , forming *6-hydroxy-5-bromopyrimidine* (E), m. 197°. Yield 94%. E with  $POCl_3$  at 145° gives *6-chloro-5-bromopyrimidine*, a nearly colorless liquid,  $b_p$  95.5°, in 51% yield. Ethylideneasparagine (F) has been prepd. and found less stable than A. F is completely dissociated in  $H_2O$  at 50°. Oxidation of F with NaOBr gave in 60% yield *6-hydroxy-5-bromo-2-methylpyrimidine-4-carboxylic acid*, colorless prismatic crystals, m. 209–10° with evolution of  $CO_2$ , forming *6-hydroxy-5-bromo-2-methylpyrimidine*, m. 231–2°. The latter gave with  $POCl_3$  *6-chloro-5-bromo-2-methylpyrimidine*, colorless liquid of penetrating aromatic odor,  $b_p$  107.5°. Benzylideneasparagine (G) was prepd. and with NaOBr gave *6-hydroxy-5-bromo-2-phenylpyrimidine-4-carboxylic acid* (K), which begins to lose  $CO_2$  at 130° without melting and goes over into *6-hydroxy-5-bromo-2-phenylpyrimidine*, m. 252°. With  $POCl_3$  this gave *6-chloro-5-bromo-2-phenylpyrimidine*,  $b_p$  193.5°, m. 130–1°, in 43% yield. The latter with Zn dust and  $H_2O$  gave 2-phenylpyrimidine,  $b_p$  157.5°, m. 128°, in 46% yield. **II. Oxidation with  $KMnO_4$ .**—This reaction is similarly carried out in alk. soln. but the yield is poor. A gives thus D, prisms, m. 268–70° with evolution of  $CO_2$ , forming C,  $b_p$  210°, m. 161°. C was also obtained by the reduction of E with Zn. Oxidation of F with  $KMnO_4$  gave *6-hydroxy-2-methylpyrimidine-4-carboxylic acid*, m. 261° with evolution of  $CO_2$ , forming *6-hydroxy-2-methylpyrimidine*,  $b_p$  200–15°, m. 212°. G gave with  $KMnO_4$  *6-hydroxy-2-phenylpyrimidine-4-carboxylic acid* (H) in 26% yield, crystals, m. 247° with evolution

of  $\text{CO}_2$ , forming 6-hydroxy-2-phenylpyrimidine,  $b_p$  245°, m. 207°. H with NaOBr gave K in 92% yield. O. B. H.

Partial substitution of acid groups in  $\beta$ -pentaacetylglucose. P. BRIGL. *Z. physiol. Chem.* 116, 1-52(1921).—1-Chloro-2-trichloroacetyl-3,5,6-triacetylglucose (A) was prepd. by heating 39 g. of  $\beta$ -pentaacetylglucose with 104 g.  $\text{PCl}_5$  for 2.5 hrs. The reaction product was transferred to a small flask and distd. at 15 mm., first at room temp. and then at 100°. The residue was stirred up with 80 cc. dry  $\text{Et}_2\text{O}$  and rubbed until the mass was homogeneous. Crystn. began soon but the material was allowed to stand on ice for 12 hrs. before filtering. The ppt. was washed with 25 cc. 90% MeOH. Yield, 16 g. After crystg. 4 times from  $\text{Et}_2\text{O}$   $[\alpha]_D^{14}$  2.95°. When dissolved in  $\text{Et}_2\text{O}$  and pptd. with petroleum ether it m. 142°. It is sol. in  $\text{C}_6\text{H}_6$ ,  $\text{CHCl}_3$ , AcOH. That 3 of the Cl atoms were present in a  $\text{CCl}_3\text{CO}$  group was proved by isolating  $\text{CCl}_3\text{CONH}_2$  as a decomn. product. The Cl in position 1 may be replaced by Ac by boiling for a few min. 5 g. of A with 15 cc. of  $\text{Ac}_2\text{O}$  containing 0.3 g.  $\text{ZnCl}_2$ .  $\alpha$ - (B) and  $\beta$ -forms (C) are produced; they can be sepd. by crystg. from  $\text{Et}_2\text{O}$ , in which the C is insol. B is sol. in  $\text{Et}_2\text{O}$  and anhyd. alc., m. 120°,  $[\alpha]_D^{14}$  101.5° (in  $\text{PhNO}_2$ ). C is sol. in  $\text{PhNO}_2$ , m. 167°,  $[\alpha]_D^{13}$  28.85°. A was reduced with Al-Hg in moist  $\text{Et}_2\text{O}$  to 1-chloro-2-monochloroacetyl-3,5,6-triacetylglucose (D). When crystd. from  $\text{Et}_2\text{O}$ -petroleum ether it m. 81°. 1-Chloro-3,5,6-triacetylglucose (E) was obtained by sapon. A with  $\text{NH}_3$  in abs. EtOH at 0°. When crystd. from AcOEt at the start  $[\alpha]_D^{13}$  25° (in  $\text{Me}_2\text{CO}$ ) but mutarotation is exhibited; it m. 158°. The presence of a free OH group in E is shown by the reaction with  $\text{SO}_2\text{Cl}_2$ . By heating for 15 min. with a 5-fold quantity of pure  $\text{SO}_2\text{Cl}_2$  and then freeing from  $\text{SO}_2\text{Cl}_2$  by distn. and finally by standing *in vacuo* with soda-lime an almost pure 2-chlorosulfonate of 1-chloro-3,5,6-triacetylglucose (F) is obtained. It decomps. in air, m. around 103°. The OH group of E may be replaced by Cl with  $\text{PCl}_5$  at 105°. The 1,2-dichloro-3,5,6-triacetylglucose (G) resulting was recrystd. from 90% alc. In  $(\text{CHCl}_3)_2$   $[\alpha]_D$  65.6°. It m. 83°. From G triacetylglucose was prepd. by shaking it with Zn dust and AcOH for 12 hrs. The product was identical with that obtained by Fischer (C. A. 8, 1121). 1-Trichloroacetyl-2,3,5,6-tetraacetylglucose (H) was prepd. by heating pure  $\text{CCl}_3\text{COCl}$  with  $\beta$ -pentaacetylglucose in  $\text{C}_6\text{H}_6$  for 4 hrs. at 100°. A little  $\text{POCl}_3$  facilitates the reaction. After distn. of the acid chloride *in vacuo* the compd. can be crystd. from  $\text{Et}_2\text{O}$ ,  $[\alpha]_D^{13}$  94.6° ( $\text{C}_6\text{H}_6$ ), m. 131°, easily sol. in  $\text{CHCl}_3$  and  $\text{C}_6\text{H}_6$ . Attempts to prep. the compd. from acetochloroglucose and  $\text{CCl}_3\text{COCl}$  were unsuccessful. That the  $\text{CCl}_3\text{CO}$  group is in position 1 was proved by prepg. acetobromoglucose from it by the action of HBr. R. L. STEHLÉ

Production and use of rare sugars. T. S. HARDING. *Sugar* 23, 671-2(1921).—The article is descriptive of the work done upon rare sugars by the Bureau of Chemistry for the purpose of supplying the American chemists with a sufficient and pure supply of materials. C. H. CHRISTMAN

History of certain rare sugars. T. S. HARDING. *Sugar* 24, 14-6(1922).—A historical sketch is given of the discovery and acquisition of additional data upon arabinose, dextrose, galactose, inulin, invert sugar, lactose, levulose, maltose, mannitol, mannose, melibiose, melizitose, raffinose, rhamnose, trehalose and xylose. C. H. CHRISTMAN

Celloisobiose. H. OST AND G. KNOTH. *Cellulosechem.* 3, 25-38(1922); cf. C. A. 14, 3656.—The crude acetate mixt. was prepd. from 60 g. cellulose, 210 g.  $\text{Ac}_2\text{O}$ , 300 g. glacial AcOH and 24 g. concd.  $\text{H}_2\text{SO}_4$  by allowing the mixt. to stand 15-17 days at 30°, the yield being 120-137%. The  $\text{Et}_2\text{O}$ - and EtOH-insol. acetate, m. 198-209°,  $[\alpha]_D$  35.8° in  $\text{CHCl}_3$ , contains the celloisobiose. The acetate is best decomd. by sapon. with 0.5 N  $\text{Ba}(\text{OH})_2$  at room temp. and the crude carbohydrate is purified by fractional pptn. with EtOH which ppts. out the dextrin. 100 parts cellulose gave 2.5 parts pure celloisobiose, containing 0.5 mol.  $\text{H}_2\text{O}$  of crystn., and forming micronedles about 0.2 mm.

long; it sinters at 155–65° and decomp. 195°. 0.4114 g. in  $H_2O$  (d. 1.0251) in a 200-mm. tube gave  $[\alpha]_D^{20}$  27.01° after 0.5 hr. and 24.42° after 23 hrs.;  $24.57^\circ \pm 0.2^\circ$  is given as the av. value. Each degree rise in temp. between 15° and 35° causes an increase in the reading of about 0.02°. Its reduction capacity is 85.3% that of cellobiose, 63.2% that of glucose and 108% that of maltose. The hydrolytic product is 2 mols. dextrose. The osazone forms small, golden yellow needles, sensitive to light, m. 165–7°, and having  $[\alpha]_{Auer} -48.4^\circ$ . Celloisobiose is not fermented by beer yeast. The acetylation in  $C_6H_5N$  at 0° or with  $AcONa$  in boiling  $Ac_2O$  gave  $\beta$ -cellobiose octaacetate, while  $H_2SO_4$  or the action of  $Ac_2O$  after boiling with  $C_6H_5N$  gave some  $\alpha$ -acetate. Thus while the carbohydrate itself is stable, in the form of its acetate it is easily rearranged to cellobiose.

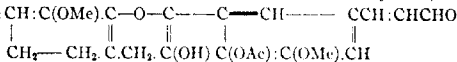
C. J. WESS

**Constitution of pine-wood lignin. II.** PETER KLASON. *Ber.* 55B, 448–55(1922); cf. C. A. 15, 860.—It was shown in the earlier paper that the greater part (about  $\frac{2}{3}$ ) of pine-wood lignin is a homogeneous substance, acrolein- or  $\alpha$ -lignin (A),  $C_{22}H_{20}O_7$ , containing a hydrolyzable Ac group, found in the sulfite waste liquor as  $AcOH$ . The residue,  $C_{22}H_{20}O_6$ , occurs in the waste liquor as the Ca salt of  $\alpha$ -lignosulfonic acid (B),  $C_{20}H_{18}O_6SO_3H$ ; this salt with  $\beta$ - $C_{10}H_7NH_2 \cdot HCl$  gives a yellow ppt. of the inner ammonium

salt  $RCH_2CH \begin{matrix} SO_3 \cdot O \\ | \\ CH = NHC_{10}H_7 \end{matrix}$  (C) ( $R = C_{17}H_{17}O_6$ );  $CaCl_2$  ppts. only B from

the waste liquor. To test the degree of homogeneity of C the fresh waste liquor was fractionally pptd. with  $NaCl$  and a  $\beta$ - $C_{10}H_7NH_2$  salt made of each of the 4 fractions and a 5th of the whole waste liquor. All 5 salts showed an av. C content of 63.97, H 5.39, S 5.73 and N 2.22%, with 0.45% ash ( $SiO_2$ ,  $Fe_2O_3$  and sulfate), and a Cl content corresponding to 0.25%  $C_{10}H_7NH_2 \cdot HCl$ ; the impurities therefore consist chiefly of about 1% of the components of the salt and are not sufficient appreciably to influence the analytical results. If the soln. is warmed with the ppt., the salt m. far below 100° to a viscous mass which solidifies on cooling to a brittle tar; this is probably a swelling phenomenon and an indication that the salt is, in part, at least, of colloidal nature. When fully dried, it is infusible. Freshly pptd. and washed, it dissolves easily in  $MeOH$  but when the soln. is allowed to stand a long time in a closed vessel it deposits on the walls a crust which is distinctly cryst., shows strong refractivity and distinct double refraction; the pptd. salt, after having stood some time under the soln., is also cryst. These facts and the above analytical results indicate that B and consequently A are homogeneous substances. When the waste liquor has stood some time a crust of  $CaSO_4$  seps. owing to the fact that, as the result of oxidation, the sulfite, bound reversibly to the aldehyde complex, is finally completely split off. But the reaction does not stop at this stage; when the waste liquor has stood a couple of years, thereby becoming dark, the  $C_{10}H_7NH_2$  salt prepd. from it contains markedly less S (5.3%) than the normal C (5.69%). The significance of lime in the sulfite cooking had already been pointed out (*Ver. Zellstoff- u. Papier-Chemiker, Hauptversammlung 1909*); lime prevents the formation of free B, which decomp. with darkening, and it is the formation of free B which is the real cause of the so-called "black cooking" (*Schwarzkothen*). When, on the other hand, the reversible sulfite is first removed from the fresh waste liquor with  $NH_4OH$  (Mitscherlich test) the  $C_{10}H_7NH_2$  salt prepd. from it has a normal S content; a salt of B can be heated even several days with concd.  $NH_4OH$  at 100° without lowering the S content of the C subsequently prepd. from it. The yellowish white  $\alpha$ -naphthylamine salt of B, almost as difficultly sol. as C, is not isomeric with C but is a normal salt,  $C_{28}H_{24}O_7 \cdot SN$ . Methylated B also yields an inner  $\beta$ -naphthylamine salt,  $C_{26}H_{22}O_6 \cdot SN$ . B in concd.  $NH_4OH$  boiled several days at 100° and freed from the excess of  $NH_3$  by evapn. gives a  $\beta$ -naphthylamine salt  $C_{26}H_{22}O_6 \cdot SN$ ; how the  $NH_3$  is attached has not yet been detd. A salt of B treated first with  $NH_4OH \cdot HCl$  and then with  $\beta$ - $C_{10}H_7NH_2 \cdot HCl$  gives at once

*β*-*naphthylamine α-ligno-oximesulfonate*,  $C_{60}H_{70}O_{14}S_2Na$ , as a white ppt. which on gentle heating of the soln. melts to a viscous light yellow mass solidifying at room temp. to a brittle resin, stable in the air, loses 5.26%  $H_2O$  at  $100^\circ$  and 8.46% at  $120^\circ$ , has no influence on polarized light but shows a cryst. appearance on strong magnification; its compn. shows beyond doubt that, at least in its salts, **B** has twice as high a mol. wt. as was previously assumed; this is in agreement with an earlier mol. wt. detn. on the Ca salt (982) made by the b. p. method. The K salt gave similar results. A f. p. detn. on the salt, however, gave 1700 and an even much higher value was obtained with the Ba salt, so that **B** seems to have a tendency to associate. If the oxime salt is heated to  $130^\circ$  it loses another mol. of  $H_2O$  and on distn. with alkali yields  $NH_3$  (40% of the amt. calcd. on the assumption that the oxime has been converted into the nitrile). With  $H_2NCONHNH_2 \cdot HCl$  **B** forms the compound  $C_{64}H_{72}O_{14}S_2N_2$ , stable in the air, does not lose its  $H_2O$  completely at  $100^\circ$ , decomps. somewhat on higher heating. Allowed to stand 45 days in 15%  $H_2O_2$  and then treated with  $\beta$ - $C_{10}H_7NH_2 \cdot HCl$ , **B** gives a compound  $C_{60}H_{72}O_{14}S_2Na$ , a white curdy ppt. gradually balling to yellowish clumps, whose compn. indicates that the CHO complex has been oxidized to  $CO_2H$  and a  $CH_2$  to a CO group. When **C** is heated 12 hrs. at  $50^\circ$  and 2 hrs. at  $100^\circ$  with  $Ac_2O$  and the product, after evapn. to dryness at  $50^\circ$  and repeated powdering and heating to  $100^\circ$  until the odor of AcOH completely disappears, is sapond. with  $N NaOH$ , 2 mols. AcOH are given off; **B** therefore contains two HO groups, only one of which can be methylated and must therefore be on a  $C_6H_5$  nucleus while the other must be attached to a group more aliphatic in nature. The Ca salt of **B** heated to about  $50^\circ$  in AcOH satd. with HCl, then dild. with much  $H_2O$  and pptd. with  $\beta$ - $C_{10}H_7NH_2 \cdot HCl$  gives a substance with 2.2% HCl, indicating that **B** contains an olefin oxide O atom, the oxide ring being partially ruptured by the HCl-AcOH. In view of the results of the oxidation with  $H_2O_2$  and of the acetylation, K. assigns to **B** the structure



instead of that proposed in the first paper.

C. A. R.

**Lignin as it occurs in the wood itself.** PETER KLASON. *Ber.* 55B, 455-6 (1922).—K. and Fagerlind had found (*Schriften Ver. Zellstoff- u. Papier-Chemiker*, No. 2) that by a long series of digestions of pine-wood alternately with  $H_2O$  and alc. (faintly acidified with AcOH, chiefly to prevent the action of the alkali from the glass) about 12% of the wood can be dissolved out. Schmidt-Nielsen believes that this is in the main an inversion process. Besides carbohydrates, P. and F. had obtained a resin (about 2% of the wood) which, after removal of the coniferous resins with petr. ether, was sepd. into a  $CHCl_3$ -sol. and an EtOH- and AcOH-sol. portion, the latter (1% of the wood) containing 59.97% C and 5.66% H. Further study of the last substance (which had been dried *in vacuo* at  $50^\circ$ ) showed that it still contained  $H_2O$  and when completely dehydrated at  $130^\circ$  contains 63.94% C and 5.74% H, which agrees well with the compn. of wood lignin (C 63.91, H 5.17%; C. A. 15, 860). Sapon. shows that a part of the Ac complex of the lignin has been split off in the prepn. of the substance but this affects the compn. only slightly. The substance gives the lignin reactions beautifully; 65% reacts with  $\beta$ - $C_{10}H_7NH_2 \cdot HCl$ ; the cooking with sulfite is not so successful, as the sintering which occurs on heating to  $100^\circ$  impedes soln., but enough can be dissolved to obtain the yellow  $\beta$ - $C_{10}H_7NH_2$  salt from the soln. The substance is therefore evidently  $\alpha$ -lignin with the unchanged acrolein complex, just as in wood; this complex is probably bound in acetal form to the hemicellulose and is set free when the latter dissolves.

C. A. R.

**Xanthosterol.** H. DIETHELM. *Arch. Pharm.* 259, 244-5 (1921).—In a recent paper (cf. C. A. 14, 1671) D. calls attention to the apparent close relationship existing between xanthosterol from the bark of *Xanthoxylon budrunga* D. C. and lupeol, a conclusion based upon various color tests and similarity in empirical compn. More recent tests



lead him to disagree with Goodson's assumption (*C. A.* 15, 2468) that xanthosterol is an impure form of lupeol.

W. O. E.

**2,3- and 2,5-Dinitro-*p*-toluidines.** JAMES SCOTT AND ROBERT ROBINSON. *J. Chem. Soc.* 121, 844-6(1922).—The nitration of 1,2,4-MeC<sub>6</sub>H<sub>3</sub>(NO<sub>2</sub>)NHAc with HNO<sub>3</sub> gives principally the 2,3-(NO<sub>2</sub>)<sub>2</sub> deriv., but in the presence of H<sub>2</sub>SO<sub>4</sub> the chief product is the 2,5-(NO<sub>2</sub>)<sub>2</sub> deriv. 2,5-Dinitro-*p*-toluidine, deep orange-red needles, m. 189°, best prepd. by hydrolyzing the acetate (aggregates of slender needles, m. 132.5°) with 10 parts H<sub>2</sub>SO<sub>4</sub> and 15 parts H<sub>2</sub>O. It is sol. to some extent in cold concd. HCl, giving a yellow soln. HNO<sub>3</sub> gives a yellow soln., from which AcONa gives a deep purple ppt. NaOH does not give this ppt. 2,3-Dinitro-*p*-toluidine, orange-yellow needles, m. 124°. Acetate, silky needles, m. 174.5°.

C. J. West

**The oxidation of trinitroxylenes.** M. GIUA. *Gazz. chim. ital.* 52, I, 183-8(1922).—Previous studies on the oxidation of nitroxylenes refer to the mono- and di-NO<sub>2</sub> derivs. by which nitrotoluic and nitrophthalic acids were obtained. Nothing is known, however, as to the relative facility with which these acids are formed and as to the influence of the NO<sub>2</sub> groups on the 2 Me groups and the 2 Me groups on each other. In this paper results on the oxidation of 1,2,3,4,6-(A), 1,3,2,4,6-(B) and 1,4,2,3,5-C<sub>6</sub>HMe<sub>2</sub>(NO<sub>2</sub>)<sub>3</sub> (C) with CrO<sub>3</sub> in concd. H<sub>2</sub>SO<sub>4</sub> are described. The 3 compds. behave differently under these conditions. The six (NO<sub>2</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>Me isomers (Koerner, Contardi, *C. A.* 9, 1478\*, 3218\*; 11, 1652; 12, 1291; Giua, *C. A.* 9, 1479, 23, 11, 484(1914)) all gave the corresponding benzoic acids with CrO<sub>3</sub>; the position of the Me group did not seem to influence the oxidation. A and C gave the corresponding toluic acids. B was not attacked under these conditions nor when heated with excess CrO<sub>3</sub> to 50-60° in concd. H<sub>2</sub>SO<sub>4</sub> but when heated to 80-90° 2,4,6-trinitrophthalic acid (D) was formed. D when heated above its m. p. or boiled in H<sub>2</sub>O loses 2 mols. of CO<sub>2</sub>, giving sym-C<sub>6</sub>H<sub>2</sub>(NO<sub>2</sub>)<sub>3</sub>. Two isomeric trinitrotoluic acids (E) might be formed from A. Only 1 was obtained and its constitution was not detd. owing to the lack of material. Only 1 of the 2 possible isomeric trinitrotoluic acids was formed from C which G. concluded is 2,3,5-trinitro-*p*-toluic acid (F) mainly because of the difficulty of esterifying it in EtOH with HCl. 5 g. o-C<sub>6</sub>H<sub>4</sub>Me<sub>2</sub> were heated some hrs. in 60 cc. HNO<sub>3</sub> (d. 1.48) + 100 cc. concd. H<sub>2</sub>SO<sub>4</sub>. The mixt. was poured into H<sub>2</sub>O and the product (6.25 g.) placed in 50 cc. fuming HNO<sub>3</sub> + 100 cc. H<sub>2</sub>SO<sub>4</sub> (20% SO<sub>3</sub>) and heated 3 hrs. at 100-10°. 5 g. of the A obtained (m. 67-8°) were dissolved in 220 cc. concd. H<sub>2</sub>SO<sub>4</sub> and treated slowly with 10 g. CrO<sub>3</sub> at 40-50°. After 1 hr. the mixt. was poured into cold H<sub>2</sub>O to sep. E; needles, m. 201-2°. The silver salt of E seps. as white needles that deflagrate on heating. 5 g. B heated similarly in H<sub>2</sub>SO<sub>4</sub> with 15 g. CrO<sub>3</sub> at 60-80° for 1 hr. gave after standing 12 hrs. unchanged B. 5 g. B with 200 cc. H<sub>2</sub>SO<sub>4</sub> and 20 g. CrO<sub>3</sub> heated 2 hrs. on the H<sub>2</sub>O bath gave after standing 36 hrs. D, small crystals, m. 196-7°. With 10% AgNO<sub>3</sub> D ppts. the yellow silver salt, which explodes on heating. C with H<sub>2</sub>SO<sub>4</sub> + CrO<sub>3</sub> at 50-60° gives some unchanged C and F as white plates, m. 230-1°; the silver salt sepd. as white needles that deflagrate on heating. 5 g. F + 5 g. PCl<sub>5</sub> + 10 cc. POCl<sub>3</sub> were heated to boiling under a condenser until HCl ceased to be evolved, the POCl<sub>3</sub> was then distd. off at reduced pressure, giving the chloride of F as a yellowish powder, which boiled with MeOH gave the methyl ester of F as needles, m. 114-5°. The Ag salt heated with EtI gave the ethyl ester of F, prisms, m. 87-8°. 2 g. of the Me ester of F heated with 20 cc. of EtOH-NH<sub>3</sub> (satd. at 0°) gave methyl 2,6-dinitro-4-methyl-5-amino-benzoate, yellow needles, m. 139-40°. The same ester treated with excess EtNH<sub>3</sub> ppts. methyl 2,6-dinitro-4-methyl-5-ethylaminobenzoate, yellow needles, m. 103-4°. B. J. W.

**Replacement of diazo groups by nitro groups.** I. V. VESELY AND K. DVORÁK. *Bull. soc. chim.* 31, 421-4(1922).—A modification of the Sandmeyer reaction is proposed, in which the aromatic amine is diazotized and then added to an excess of Gattermann's

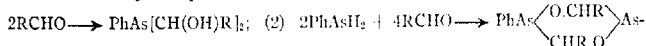
mol. Cu and aq.  $\text{NaNO}_2$ . The yields of  $\text{NO}_2$  deriv. reported are:  $p\text{-BrC}_6\text{H}_4\text{NO}_2$  from  $p\text{-BrC}_6\text{H}_4\text{NH}_2$ , 61.4%;  $\text{PhNO}_2$  from  $\text{PhNH}_2$ , 42.5%;  $\beta\text{-C}_{10}\text{H}_7\text{NO}_2$  from  $\beta\text{-C}_{10}\text{H}_7\text{NH}_2$ , 28.2%. Cu bronze may be used in place of mol. Cu.

A. W. DOX

**Colloidal trimercuracetanilide acetate.** G. ROSSI. *Gazz. chim. ital.* **52**, I, 189-92 (1922).—In 2 previous papers R. and Raffo (*Gazz. chim. ital.* **42**, II, 623; **44**, I, 109; *C. A.* **7**, 1259; **8**, 2775) described 2 colloidal organo-Hg derivs. of  $\text{PhNHAc}$ : *i. e.*, tetra- and pentamercuracetanilide acetates. Since the corresponding derivs. with 1, 2, 4 and 5  $\text{HgOAc}$  groups are now known it was of interest to prep. the *trimercuracetanilide acetate* (A) which is described here. 10.08 g.  $\text{Hg}(\text{OAc})_2$  + 2.70 g.  $\text{PhNHAc}$  in a tube was heated at  $140^\circ$  until it boiled and evolved  $\text{HOAc}$  and began to thicken. On cooling the product A assumed a glass-like appearance; in  $\text{H}_2\text{O}$  it softened and gave a viscid brown liquid. On adding  $\text{Me}_2\text{CO}$  to the soln. A ppts. and when dried over  $\text{H}_2\text{SO}_4$  *in vacuo* gives a friable glassy mass that decomp. above  $180^\circ$ . Treated with excess Br in KBr soln. it gives *trimercuracetanilide bromide* at first. This decomp., giving a red paste which, crystd. from EtOH, gives tribromoacetanilide as white needles, m.  $188-9^\circ$ . A gives typical colloidal solns. that foam like albumins, do not dialyze and coagulate with heat and is therefore analogous to the tetra- and penta-derivs. The mol. wts. of these compds. are: 393, 651, 909, 1167 and 1425 for the mono-, di-, tri-, tetra- and penta-derivs., resp. The last 3 are colloidal and the whole series shows that with increasing mol. wt. the facility of giving colloidal solns. is increased. The colloidal solns. of the 3-, 4- and 5-derivs. do not have the same properties and stability. While all coagulate with heat the soln. of A is most stable. The solns. of A do not ppt. with EtOH or AcOH but sep. on adding  $\text{Me}_2\text{CO}$ , while the tetra-deriv. is pptd. by  $\text{Me}_2\text{CO}$  and EtOH but not by AcOH and the penta-deriv. is pptd. by all 3. AcOH is certainly the stabilizer for the 4- and 5-derivs.; in fact when it is eliminated by dialysis they coagulate. It could not be shown that AcOH is the crystalloid stabilizer for A but R. believes this may be true.

E. J. WITZEMANN

**Reactions of the arsines. II. Condensation of aromatic primary arsines with aldehydes.** C. S. PALMER WITH ROGER ADAMS. *J. Am. Chem. Soc.* **44**, 1356-82 (1922); cf. *C. A.* **15**, 673.—A further study of the reaction between  $\text{PhAsH}_2$  and aldehydes has shown that it may take place in 3 ways, depending on the conditions: (1)  $\text{PhAsH}_2$  +



Ph (A) +  $2\text{RCH}_2\text{OH}$ ; (3)  $\text{PhAsH}_2 + 2\text{RCHO} \longrightarrow \text{PhAs:AsPh} + 2\text{RCH}_2\text{OH}$ . (1) takes place readily and gives 60-95% yields when  $\text{PhAsH}_2$  and an excess of an aromatic or aliphatic aldehyde and a little concd. HCl, with or without a solvent, are stirred vigorously together, the temp. being kept down with ice water; with aromatic aldehydes the best results are obtained with anhyd. HCl gas. The products are generally oils in the aliphatic and solids in the aromatic series and are quite stable towards  $\text{H}_2\text{O}$ , dil. hot or cold alkalis and cold dil. acids; the aliphatic and some of the aromatic compds. oxidize slowly in the air to an arsonic acid and the aldehyde; the oxidation proceeds much more rapidly in a solvent ( $\text{CCl}_4$ ); oxidizing agents ( $\text{KMnO}_4$ ,  $\text{HNO}_3$ ) produce the same oxidation in both the aliphatic and aromatic derivs. The aliphatic compds. may be titrated quant. in  $\text{Et}_2\text{O}$  with I according to the equation  $\text{RAs}[\text{CH}(\text{OH})\text{R}]_2 + 2\text{I} = \text{RAsI}_2 + 2\text{HI} + 2\text{RCHO}$ ; the aromatic compds. react slowly with I but quant. titration is impossible. The compds. are decidedly stable towards reducing and dehydrating agents (except anhyd. HCl, acid chlorides or anhydrides under certain conditions). The aliphatic derivs. form unstable addition products with halogen acids and characteristic stable chloroplatinates. They do not yield  $\text{CH}_4$  or  $\text{C}_2\text{H}_4$  with  $\text{MeMgI}$  or  $\text{EtMgI}$ . The non-formation of normal derivs. of the  $\text{HO}$  groups with acid chlorides and anhydrides can be explained by the fact that certain dehydrating agents ( $\text{AcCl}$ ,  $\text{Ac}_2\text{O}$ , even anhyd.

HCl) easily bring about a secondary reaction, 2 mols. of the HO compd. losing 2 mols. alc. with formation of tetrahydro-1,4,2,5-dioxiarsines (A); these are obtained directly according to reaction (2) by allowing the arsine and aldehyde to stand 1-2 days at room temp. in the presence of anhyd. HCl. No such ring compds. have as yet been obtained with aromatic aldehydes. They are not affected by long standing with  $H_2O$ , dil. acids or alkalis or even hot 10% alc. KOH; they oxidize in the air to arsine oxides and the aldehydes and under the influence of oxidizing agents to arsonic acids and the aldehydes or their oxidation products; they react with I but cannot be titrated quant., form chloroplatinates and chlorocuprates stable in the air but no halogen acid addition products, are converted by  $PCl_3$  into dichloroarsines and aldehydes. Reaction (3) takes place when a higher temp. is used with or without a catalyst or when the arsine and aldehyde are allowed to stand a long time at room temp. without a catalyst. Detailed directions are given whereby  $PhAsO_3H_2$ , softens  $158^\circ$ , passing into the anhydride, may be prepd. in 800-1,000 g. yield from 1 kg.  $As_2O_3$  and 744 g.  $PhNH_2$  and  $PhAsH_2$  in 50-83% yield from the  $PhAsO_3H_2$ ; the  $PhAsH_2$   $b_{78}$   $93^\circ$ ,  $d_{25}^{25}$  1.349,  $n_D^{25}$  1.6082. *Bis-[ $\alpha$ -hydroxyethyl]phenylarsine* (127 g. from 100 g.  $PhAsH_2$ , 2 cc. concd. HCl and 75 g.  $AcH$  or paraldehyde),  $b_{21}$   $175-6^\circ$ ,  $d_{25}^{25}$  1.252,  $n_D^{25}$  1.5619; *bis- $\alpha$ -hydroxypropyl homolog* (28 g. from 17 g.  $EtCHO$ ),  $b_{24}$   $196-7^\circ$ ,  $d_{25}^{25}$  1.176,  $n_D^{25}$  1.5425; *butyl compound* (75 g. from 50 g.  $PrCHO$ ),  $b_{18}$   $187^\circ$ ,  $d_{25}^{25}$  1.116,  $n_D^{25}$  1.5271; *isotoleryl compound* (yield, 50%),  $b_4$   $170^\circ$ ,  $d_{25}^{25}$  1.079,  $n_D^{25}$  1.5202, needles from  $Et_2O$ , m.  $62^\circ$ ; *heptyl compound*,  $b_2$   $263-4^\circ$  (considerable decompn.),  $d_{25}^{25}$  1.069,  $n_D^{25}$  1.4650, solidifies in a freezing mixt.; *benzyl compound* (obtained practically quant. from 58 g.  $BzH$ , 40 g.  $PhAsH_2$  and dry HCl in 300 cc.  $Et_2O$ ), silky needles from  $PhCl$ , m.  $193^\circ$ ; *p-chlorobenzyl compound* (yield, 40%), needles from  $PhCl$ , m.  $164^\circ$ ; *p-methoxybenzyl compound*, yellowish oil; *bis-[o-(carboxymethoxy)- $\alpha$ -hydroxybenzyl]phenylarsine*,  $PhAs[CH(OH)C_6H_4OCH_2CO_2H]_2$  (42 g. from 30 g.  $o-HOCH_2C_6H_4OCH_2CO_2H$ ), m.  $145-7^\circ$  (loss of  $CO_2$ ). *2,5-Diphenyltetrahydro-1,4,2,5-dioxiarsine* (about 10 g. from 15 g.  $PhAsH_2$  with paraformaldehyde and concd. HCl),  $b_2$   $215-6^\circ$ ,  $d_{25}^{25}$  1.547,  $n_D^{25}$  1.6522. The following homologs were also prepd.: *3,6-Dimethyl*, prepd. like the preceding compd. or by heating  $PhAs[CH(OH)Me]_2$  and 0.5 part  $Ac_2O$  at  $140-50^\circ$  under a reflux for 7 hrs. or by allowing the  $PhAs[CH(OH)Me]_2$  to stand a few days in the presence of anhyd. HCl,  $b_{10}$   $257^\circ$  (slight decompn.),  $d_{25}^{25}$  1.369,  $n_D^{25}$  1.6332; *3,6-diethyl*, obtained crude practically quant. from  $PhAsH_2$  and  $EtCHO$  but pure in only about 25% yield owing to decompn. during distn.,  $b_2$   $212^\circ$ ,  $d_{25}^{25}$  1.336,  $n_D^{25}$  1.6217; *3,6-dipropyl*,  $b_2$   $241-2^\circ$  (considerable decompn.),  $d_{25}^{25}$  1.297,  $n_D^{25}$  1.5856; *3,6-diisobutyl* (5.5 g. from 8 g.  $PhAsH_2$  and 9 g. *iso-BuCHO*), purified by discarding all of the product which  $b_{10}$  below  $240^\circ$ , dissolving the residue in  $Me_2CO$ , filtering through charcoal and evapp. the  $Me_2CO$ , is a nearly colorless oil,  $d_{25}^{25}$  1.296,  $n_D^{25}$  1.5869; *3,6-difuryl*, obtained quant., resembles Zn dust when powdered, burns without melting and is insol. in all solvents. *p-ClC\_6H\_4AsO\_3H\_2*, decomps. about  $348^\circ$ , is readily obtained in 160-200 g. yield from 126 g. *p-ClC\_6H\_4NH\_2* by a method described in detail; 70 g. in  $MeOH$  with amalgamated Zn and HCl gives in 3-7 days 16-26 g. pure *p-chlorophenylarsine* (B),  $b_{21}$   $116^\circ$ ,  $b_{20}$   $159^\circ$ , thin leaves from  $Et_2O$ , m.  $30.5-0.7^\circ$ ,  $d_{25}^{25}$  1.507,  $n_D^{25}$  1.6143. *Bis-[ $\alpha$ -hydroxybenzyl]-p-chlorophenylarsine*, obtained in small yield from B and 2 mols.  $BzH$  with a little concd. HCl, long silky needles from  $PhCl-EtOH$ , m.  $218-8.5^\circ$ ; *bis- $\alpha$ -hydroxyethyl compound*,  $b_{21}$   $183^\circ$ ,  $d_{25}^{25}$  1.336,  $n_D^{25}$  1.5728. *o-Chlorophenylarsonic acid* (yield, 60-75%), m.  $186-7^\circ$ . *o-Chlorophenylarsine* (yield, 45-60%), b.  $206^\circ$ ,  $d_{25}^{25}$  1.519,  $n_D^{25}$  1.6250. *Bis-[ $\alpha$ -hydroxybenzyl]-o-chlorophenylarsine*, crystals from  $EtOH$  or  $Et_2O$ , m.  $146-7^\circ$ . *p-MeC\_6H\_4AsO\_3H\_2* is obtained in 50-65% yield and gives 30-50% *p-tolylarsine*, plates, m.  $20^\circ$ ,  $b_{11}$   $113.5^\circ$ ,  $d_{25}^{25}$  1.295,  $n_D^{25}$  1.5891. *Bis-[ $\alpha$ -hydroxybenzyl]-p-tolylarsine*, long needles from  $C_6H_5EtOH$ , m.  $208^\circ$ ; *bis- $\alpha$ -hydroxyethyl compound* (yield, 80%),  $b_{21}$   $176-7^\circ$ ,  $d_{25}^{25}$  1.2331,  $n_D^{25}$  1.5570, oxidizes readily in the air. *o-MeC\_6H\_4AsO\_3H\_2* (yield, about 40%), m.  $159-60^\circ$ .

*o*-Tolylarsine,  $b_m$  121°,  $d_{25}^{25}$  1.301,  $n_D^{25}$  1.5925, oxidizes rapidly in the air to the *arseno compound*, crystals from  $C_6H_6$ , m. 205–8°. *Bis*-[ $\alpha$ -hydroxybenzyl]-*o*-tolylarsine, needle-like crystals from  $Et_2O$ , m. 140°; *bis*- $\alpha$ -hydroxyethyl compound,  $b_m$  165°,  $d_{25}^{25}$  1.244,  $n_D^{30}$  1.5573, has a somewhat greater tendency to oxidize than other analogous compds. The compds.  $PhAs[CH(OH)R]_2$  when heated over a free flame decomp. into  $PhAsH_2$  and  $RCHO$ ; the  $PhAsH_2$  at once oxidizes in the presence of air to  $PhAs:AsPh$  and the latter changes completely into  $Ph_2As$  and  $As$ . With  $EtI$  under a reflux is obtained  $PhAsO$ ;  $PCl_5$  gives  $PhAsCl_2$ ,  $HCl$ ,  $PCl_3$  and  $RCHO$ ;  $PhAsCl_2$  yields  $PhAs:AsPh$ ,  $HCl$  and  $RCHO$ .  $PhAs[CH(OH)Me]_2$  with const. boiling  $HI$  gives a *hydriodic acid addition product*  $C_{10}H_{10}O_2As.HI$ , yellow powder, m. 94–6°, stable to alkalis but soon changes to a pasty mass in the air (*butyl compound*, m. 157–8°); *hydrobromic acid addition product*, m. 117–8° (*butyl compound*, m. 111–2°). *Bis*-[ $\alpha$ -hydroxyethyl]phenylarsine chloroplatinate, m. 169–70°; *propyl compound*, m. 148–9°; *butyl compound*, m. 119–21°; *isovaleryl compound*, m. 84–5°. *3,6-Dimethyl-2,5-diphenyltetrahydro-1,4,2,5-dioxiarsine chloroplatinate*, m. 130–1°; *3,6-diisobutyl compound*, m. 76–7°. *3,6-Dimethyl-2,5-diphenyltetrahydro-1,4,2,5-dioxiarsine chlorocuprate*, m. 150–2°; *3,6-diisobutyl compound*, m. 78–9°.  $PhAsH_2$  (7.5 g.) heated under a reflux 2 hrs. in  $AcOH$  in a  $CO_2$  atm. with 5 g.  $BzH$  gives 6.75 g.  $PhAs:AsPh$  and  $PhCH_2OAc$ ; the same reduction occurs when  $PhAsH_2$  is heated in a sealed tube at 100° with  $BzH$  and even in the presence of concd.  $HCl$ , the condensation reaction being entirely prevented at 100°. Similarly 6.5 g. *p*- $MeOC_6H_4CHO$  heated 6 hrs. at 100° in a sealed tube with 7.5 g.  $PhAsH_2$  and 5 g.  $NaOAc$  gives 6 g.  $PhAs:AsPh$  and  $MeOC_6H_4CH_2OH$ : 9 g. *p*- $ClC_6H_4CHO$ , 10 g.  $PhAsH_2$  and 1 g. fused  $ZnCl_2$  allowed to stand 5 days in  $C_6H_6$  yield 10 g.  $PhAs:AsPh$  and 9 g. *p*- $ClC_6H_4CH_2OH$ ;  $PhNHNHPh$  is obtained from  $PhNO_2$  and  $PhAsH_2$  allowed to stand overnight in  $Et_2O$ ;  $PhCH:Cl:CHO$  reacts vigorously with  $PhAsH_2$  and even in the presence of concd.  $HCl$  reduction occurs with formation of  $PhAs:AsPh$  and  $PhCH:CHCH_2OH$ ; crotonic and salicylic aldehydes are similarly reduced;  $CCl_3CHO$  and the hydrate react violently with formation of  $PhAsCl_2$  and  $AcH$ . C. A. R.

**Action of magnesium methyl iodide on mercuriated aromatic ketones and on mercuric chloride.** A. ABELMANN. *Ber. pharm. Ges.* 31, 240–7 (1921); cf. Abelman, *C. A.* 9, 314; Grignard, *C. A.* 10, 1525.— $MeMgI$  and  $HgCl_2$  react in  $Et_2O$  at a moderate temp. with the formation of  $MeHgI$ , leaflets, m. 147°. The same compd. also results by the action of  $MeMgI$  on acetophenone mercurichloride together with a small amt. of  $AcPh$  and the substance  $(HOCMePhCH_2)_2Hg$ , which turns yellow at 130° and sublimes at 150°, while the analogous substance  $(HOCMePhC_6H_4)_2Hg$ , m. 130° (decomp. 110°), is obtained from benzophenone mercurichloride. The primary product of the reaction is apparently the compd.  $HOCMePhCH_2HgCl$ , from 2 mols. of which the mercuriated substance above noted results through loss of a mol. of  $HgCl_2$ , the latter being thereupon changed into  $MeHgI$ .  $AcPh$  results from hydrolysis of the compd.  $HOCMePhCH_2HgCl$ . Elementary analyses of these substances must be carried out with  $PbCrO_4$ . W. O. E.

**The speed of sulfonation of phenols. I. The effect of temperature and the methyl group.** A. F. CAMPBELL. *J. Chem. Soc.* 121, 847–57 (1922).—The influence of the introduction of the  $Me$  group into the  $PhOH$  mol. on the velocity of sulfonation varies with the relative position of the  $Me$  to the  $HO$  group and also, but to a different degree, with the temp. The  $Me$  group in either the *o*- or *p*-position to the  $HO$  group retards the speed of sulfonation at all temps. from 20 to 80°. An *o*- $Me$  group retards the speed to the least extent and, at 20°, to approx.  $1/3$  the degree of a *p*- $Me$  group. As the temp. of sulfonation increases, the retarding influence of the *o*- $Me$  group diminishes somewhat rapidly up to about 60°. Above this temp. the influence is only very slightly progressive. At 80° and above the difference in the comparative speed of sulfonation of  $PhOH$  and *o*- $MeC_6H_4OH$  is almost a constant. While the  $Me$  group in the *o*- and *p*-positions to the

HO has the same general effect at all temps., the *m*-Me group both accelerates and retards the speed of sulfonation accordingly as the reaction is carried out at a lower or higher temp. The speed is accelerated at temps. below 65°, when the rate for *m*-MeC<sub>6</sub>H<sub>4</sub>OH and PhOH are approx. the same; above this the rate is retarded. *o*- and *m*-MeC<sub>6</sub>H<sub>4</sub>OH are sulfonated at approx. the same rate at 70°. The separate effects of the *m*- and *p*-Me groups reach an equil. point at about 100°, where the 2 isomers are sulfonated at the same rate. At 20° the order of sulfonation is *m*-MeC<sub>6</sub>H<sub>4</sub>OH, PhOH, *o*- and *p*-MeC<sub>6</sub>H<sub>4</sub>OH. Phenol is sulfonated at 2.11 times the rate of *p*-MeC<sub>6</sub>H<sub>4</sub>OH and 2.21 times the rate of *m*-MeC<sub>6</sub>H<sub>4</sub>OH at 40°. *o*-MeC<sub>6</sub>H<sub>4</sub>OH is sulfonated at 0.859 times the rate of PhOH at 40° and *p*-MeC<sub>6</sub>H<sub>4</sub>OH at 1.085 times that of PhOH at 40°.

C. J. WEST

**Cumulative effect of the chlorine atom and the methyl and sulfonyl chloride groups on substitution in the benzene nucleus. III.** WILLIAM DAVIES. *J. Chem. Soc.* 121, 785-91 (1922); cf. *C. A.* 15, 2847.—The nitration of 1,2,6-MeC<sub>6</sub>H<sub>3</sub>(SO<sub>2</sub>Cl)Cl (Wynne, *J. Chem. Soc.* 61, 1040) under conditions employed in previous expts. leads to the formation of 90% of 6-chloro-5-nitro-*m*-toluenesulfonyl chloride, long prisms, m. 49-50°. Boiling with alc. alkali or N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O gives characteristic colorations. *Amide*, small needles from alc., m. 201-2°. *Sodium salt*, prepd. by boiling the chloride with alc., and titrating the free acid with NaOH, anhydrous scales, readily sol. in cold and extremely sol. in hot H<sub>2</sub>O. The *potassium salt*, glistening scales, is sparingly sol. in cold and slightly sol. in hot H<sub>2</sub>O. *Ammonium salt*, needles, slightly sol.; *rubidium salt*, needles, less sol. than the acid tartrate; *cesium salt*, needles, almost as sol. as the Na salt; *magnesium salt*, very sol.; *barium salt*, needles, slightly sol. in cold, readily sol. in hot H<sub>2</sub>O. Boiled with an excess of NaOH, the chloride gives 1,3,5,6-MeC<sub>4</sub>H<sub>2</sub>(SO<sub>2</sub>H)(OH)NO<sub>2</sub>, which, with dil. HNO<sub>3</sub>, gives 3,5-(O<sub>2</sub>N)<sub>2</sub>C<sub>6</sub>H<sub>2</sub>(OH)Me. *Neutral barium salt*, scarlet powder, sparingly sol. in H<sub>2</sub>O; acid *barium salt*, spherical clusters of needles, readily sol. in boiling H<sub>2</sub>O. *Neutral sodium salt*, thick orange-red prisms, readily sol. in hot H<sub>2</sub>O; *acid salt*, minute crystals. *Neutral lead salt*, orange microcrystals, sparingly sol. in hot H<sub>2</sub>O. *Acid silver salt*, needles, moderately sol. in H<sub>2</sub>O. These results indicate that the Cl atom has, as far as nitration is concerned, a much greater directing effect in this type of trisubstituted C<sub>6</sub>H<sub>3</sub> deriv. than is generally supposed (cf. Robinson, *C. A.* 12, 135).

C. J. WEST

**An instance of the apparent effect of the entering group on the position of substitution in the benzene nucleus.** WILLIAM DAVIES. *J. Chem. Soc.* 121, 806-15 (1922); cf. preceding abstr.—The monochlorination of 2,4-Cl(O<sub>2</sub>N)C<sub>6</sub>H<sub>3</sub>Me with SbCl<sub>5</sub> or FeCl<sub>3</sub> as catalyst leads to a mixt. of isomers, containing more than 30% of the 2,6-Cl<sub>2</sub> deriv. When compared with the nitration of 2,4-Cl(O<sub>2</sub>N)C<sub>6</sub>H<sub>3</sub>Me, in which more than 85% of the product is the 4,5-(NO<sub>2</sub>)<sub>2</sub> deriv., the result seems to show that either the nature of the entering group or the catalyst employed in the chlorination has a considerable effect on the position of substitution. 2,6-Dichloro-4-nitrotoluene (A), thick, faintly odorous, blunt needles, m. 65°, b<sub>760</sub> 278-0°, by the use of SbCl<sub>5</sub>, FeCl<sub>3</sub> or Al-Hg as catalyst; it is very stable towards KMnO<sub>4</sub>. 2,6-Dichloro-3,4-dinitrotoluene (B), by nitration of A with mixed HNO<sub>3</sub>-H<sub>2</sub>SO<sub>4</sub>, long needles, m. 130-1°. Reduction of A with Fe filings gave 2,6-dichloro-*p*-toluidine, needles, m. 56-7°; *hydrochloride*, long needles; *acetate* (C), slender needles, m. 220°. Diazotized and treated with β-C<sub>10</sub>H<sub>7</sub>OH, it gives 2,6-dichloro-toluene-4-*α*-20-β-naphthol, minute crimson rods, m. 243°. The nitration of C by means of concd. HNO<sub>3</sub> gave 2,6-dichloro-3-nitroaceto-*p*-toluidide, needles, m. 180°, which are sapond. to 2,6-dichloro-3-nitro-*p*-toluidine (D), minute orange needles, m. 130-1°. *Hydrochloride*, clusters of needles. D, upon diazotizing and heating upon the H<sub>2</sub>O bath, gave 2,6,3,5-C<sub>6</sub>H<sub>2</sub>Cl<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub> (E). E, heated with a mixt. of HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> at 140-50° for 6 hrs., gave 2,6-dichloro-3,4,5-trinitrotoluene, small needles, m. 160-3°. This reacts

with alc.  $\text{NH}_3$ , the  $\text{NO}_2$ -groups apparently being replaced by  $\text{NH}_2$ -groups, but a pure product was not isolated.

C. J. WEST

**Addition compounds of the sym-trinitroanisole with the tertiary bases.** M. GIUA. *Gazz. chim. ital.* 52, I, 182(1922).—In a preceding note (*C. A.* 16, 77) G. described these derivs. but omitted to mention that Kohn and Grauer (*C. A.* 8, 500; *J. prakt. Chem.* [2] 91, 468(1915)) and Walther (*C. A.* 9, 2065) had previously obtained several of them. The pyridine-trinitroanisole addition compd. gives pyridine metho-chloride chloroplatinate  $(\text{C}_5\text{H}_5\text{N}.\text{MeCl})_2\text{PtCl}_6$ , m. 205–7°, in  $\text{EtOH}$  with  $\text{PtCl}_4$ . W. obtained the same compd. from pyridine-trinitrophenol by the same treatment. E. J. WITZEMANN

**Nitro derivatives of *p*-phenetidine.** F. REVERDIN AND A. ROETHLISBERGER. *Helvetica Chim. Acta* 5, 300–14(1922). **Part I.**—In the earlier work (cf. *C. A.* 7, 3314) it was found that in 2,3,5-trinitro-*p*-phenetidine (A) the  $\text{NO}_2$  group in the 2-position was readily replaced by  $\text{NH}_2$ , OH,  $\text{NMe}$ , OPh just as with the similar anisidine deriv. (cf. *C. A.* 4, 2648; 7, 1712). The present work is upon the effect of acylation upon the mobility of the  $\text{NO}_2$  group in A and also upon the 2,3-dinitro-*p*-phenetidine (B) from the same standpoint. B is best prepd. by going through the nitration of toluenesulfonyl-*p*-phenetidine (C), using 5 parts  $\text{HNO}_3$  (d. 1.48) below  $-12^\circ$ . After all the C is added, warm to  $18^\circ$  for 20 min., and after crystn. has set in, drown in ice water, filter, wash and dry. Yield 80%, m. 145–6°. Sapond. with concd.  $\text{H}_2\text{SO}_4$ , it yields B. From the wash waters in the above nitration there was obtained a small amt. of the 2,5-deriv., which on sapon. gave 2,5-dinitro-*p*-phenetidine (D), m. 139.5°. For identification this was converted to 2,5-( $\text{O}_2\text{N}$ ) $_2\text{C}_6\text{H}_3\text{OEt}$ , m. 96–8°, and further to 2,5-( $\text{O}_2\text{N}$ ) $_2\text{C}_6\text{H}_3\text{OH}$ , m. 105.5°. Heated with concd.  $\text{H}_2\text{SO}_4$  40 min. D splits off  $\text{Et}$  (although the similar Me deriv. is stable), forming 2,5-dinitro-*p*-aminophenol, m. 166–7°. The acetyl derivative of this compd. gave from alc. a mixt. of yellow and red crystals. The yellow crystals on heating become red and m. 144–5°. This is then another case of the *chromoisomerism* of the nitrophenols. It was likewise observed that 3-nitrotoluenesulfonyl-*p*-phenetidine (G) exists in two forms, one pale yellow, m. 104–5°, and the other deep yellow, m. 94–5°. Similarly 2,3-dinitrotoluenesulfonyl-*p*-phenetidine (E) was found to exist as pale yellow needles m. 145–6° and as colorless cubes m. 162–3°. **Part II.** In the course of the work several other new derivs. have been prepd.: 2,3-dinitro-*N*-methyltoluenesulfonyl-*p*-phenetidine, m. 152.5°, 2,3-dinitro-*N*-benzoyltoluenesulfonyl-*p*-phenetidine (F), m. 182–3°, 2,3,5-trinitro-*N*-benzoyltoluenesulfonyl-*p*-phenetidine, m. 246–7° (decompn.). With regard to the mobility of the  $\text{NO}_2$  groups in B there was found no reaction with  $\text{NH}_3$ ,  $\text{Et}_3\text{NH}$ ,  $\text{PhNH}_2$ , although the acyl derivs. E and F readily split out  $\text{NO}_2$ . R. and R. prepd. thus 2-nitro-3-phenylamino-*N*-toluenesulfonyl-*p*-phenetidine, ruby-red needles, m. 111.5°, 2-nitro-3-phenylamino-*N*-benzoyl-*p*-phenetidine, dark brown crystals, m. 153.4°, 2-nitro-3-phenylamino-*N*-acetyl-*p*-phenetidine, light brown crystals, m. 151–2°, and 2-nitro-3-methylamino-*N*-benzoyl-*p*-phenetidine, dark brown crystals, m. 135–6°. In the case of the acyl derivs. of A it was found the mobility of  $\text{NO}_2$  was unchanged. The new derivs., 2-phenylamino-3,5-dinitro-*N*-toluenesulfonyl-*p*-phenetidine, yellow prisms, m. 198–9°, and 2-methoxy-3,5-dinitro-*N*-toluenesulfonyl-*p*-phenetidine, orange needles, m. 120–1°. Finally there have been prepd. a no. of highly colored addition products of G, E, and 2,3,5-trinitrotoluenesulfonyl-*p*-phenetidine with various amines, i. e.,  $\text{MeNH}_2$ ,  $\text{Me}_2\text{NH}$ ,  $\text{Me}_3\text{N}$ ,  $\text{EtNH}_2$ ,  $\text{Et}_2\text{NH}$ ,  $\text{PhNH}_2$ , and quinoline. The products were only stable in a sealed flask. For greater details see Roethlisberger, *Diss. Univ. Geneva*.

O. B. H.

**Facts and theory in the constitution of the hydroxyazo compounds.** E. PUXEDDU AND MARCELLA GENNARI. *Gazz. chim. ital.* 52, I, 216–29(1922).—This paper constitutes a review of the most important facts concerning the constitution of the hydroxyazo compds. All attempts during the past 30 years to develop a single structural

formula for the 3 possible series, *o*-, *m*- and *p*-hydroxyazo compds., have merely helped to differentiate the compds. of the *o*- series from those of the *m*- and *p*-series. This effort was in part due to their identical methods of prepn., and to a reluctance to admit the quinonic structure for the *o*- and not for the *p*-series when *p*-quinones are so much more frequently met with. The insolubility of the *o*-series in the calcd. (or even excess) amt. of alkali is an obstacle to classifying them among phenolic compds. The behavior of the acyl derivs. on reduction is certain evidence for the azophenolic structure of the *p*-series and for the hydrazone constitution of the *o*-series in spite of certain existing views on the migration of aminic and iminic H in their compds. The proof of the instability of the quinonoid nucleus in the acyclic derivs. of the *o*-hydroxyazo compds. needs to be supported by more decisive results. The test with the isocyanate that served for such a long time to establish a sharp differentiation between the *o*- and *p*-series is not distinctive any longer since it was shown that even the *o*-compds. react after several weeks like the *p*-derivs. But this delayed action is certain proof of their difference and indicates that the action of the isocyanate on the *o*-compds. may be 2-fold: 1st, a transformation into the azophenolic form and, 2nd, an addition in the usual way. The physical chem. behavior also indicates a difference in constitution between the *o*- and *p*-derivs. as indicated by f. p. detns. and other facts. On the basis of all the known facts the constitution of these compds. is summarized as follows: (I) The hydroxyazo compds. both in the free state and as their acyclic derivs. behave like tautomeric compds. (II) The *p*-hydroxyazo compds. both in the free state and as the acyl derivs. are always compds. of the phenolic type. The *m*-hydroxyazo compds. behave similarly. (III) The *o*-hydroxyazo compds., on the contrary, both in the free state and as their acyl derivs. have the quinone hydrazone structure with a marked tendency to pass to the more stable azophenolic arrangement. (IV) The mesohydric formula proposed by Oddo in so far as it gives a representation of the desmotropic phenomenon is not only acceptable but gives a simple intuitive scheme applicable to all analogous phenomena. E. J. W.

**The degree of hydrolysis of the alkali salts of the hydroxyazo compounds.** E. PUXEDDU. *Gazz. chim. ital.* **52**, I, 235-8(1922).—Earlier results are reviewed that show that the common methods of detg. the degree of hydrolysis can not be applied to the alkali salts of the hydroxyazo compds. since the presence of the free base which seps. after hydrolysis interferes. Cond. detns. on Na and K benzeneazophenol and Na benzeneazo-*o*-cresol (A) showed by the continual increase in the cond. of the solns. kept in the dark and at 25° that the equil:  $\text{PhN:NC}_6\text{H}_4\text{ONa} + \text{H}_2\text{O} \longrightarrow \text{PhN:NC}_6\text{H}_4\text{OH} + \text{NaOH}$  changes owing to the sepn. of increasing amts. of the hydroxyazo compd. P. then tried to det. the degree of hydrolysis by extg. the free hydroxyazo compd. quickly with  $\text{Et}_2\text{O}$ . The  $\text{Et}_2\text{O}$  soln. was sepd., quickly dried with  $\text{Na}_2\text{SO}_4$ , evapd. in a Pt dish and weighed. Concordant results were obtained with A, Na benzeneazo-*p*-phenol (B) and Na *o*-tolueneazophenol (C), which are given in a table. With 0.3657 g. A per 50 cc. 30.87% were hydrolyzed at 15°; with 0.3439 g. B per 50 cc. 33.24% were hydrolyzed and with 0.3657 g. C 34.39% were hydrolyzed. E. J. WITZEMANN

**Hydroxybenzoylphloroglucinols.** HIDEJIRO NISHIKAWA AND ROBERT ROBINSON. *J. Chem. Soc.* **121**, 830-43(1922).—This work was undertaken in connection with the constitution of aromadendrin, found in the kino of certain eucalyptus. 2,4,6,2'-Tetrahydroxydiphenyl ketimine (cf. Karrer, *C. A.* **16**, 716), by condensing phloroglucinol (A) and *o*- $\text{HO}_2\text{C}_6\text{H}_4\text{CN}$ , golden yellow needles, does not m. 300°. Hydrochloride, needles. The corresponding ketone could not be obtained. Hydrolyzed with NaOH, 1,3-dihydroxyxanthone is formed, glistening needles, m. 259° (Kostanecki and Nessler, *Ber.* **24**, 2980, give 247°). 2,4,6,3'-Tetrahydroxybenzophenone, from *m*- $\text{HO}_2\text{C}_6\text{H}_4\text{CN}$  and A, followed by hydrolysis, pale yellow, thin, narrow leaflets, decomp. 246°.  $\text{FeCl}_3$  gives a purple soln., NaOH orange. 2,4,6,4'-Tetrahydroxybenzophenone, from *p*- $\text{HO}_2\text{C}_6\text{H}_4\text{CN}$ ,

through the *ketimine sulfate* (short yellow needles), pale brown prisms with 2 H<sub>2</sub>O, m. 210° to a deep red liquid. The color with FeCl<sub>3</sub> is brown, with alkalis yellow. C. J. W.

**Some derivatives of anisic acetone.** EMILIEN LE BRAZIDEC. *Bull. soc. chim.* **31**, 255-65 (1922).—B. prepd. *p*-MeOC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>COMe (A) by Balbiano's method. HOC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>COCH<sub>3</sub> (B) was made from A by demethylating with HBr in AcOH. B is sol. in alc., benzene, Et<sub>2</sub>O, CHCl<sub>3</sub> and Ac<sub>2</sub>O, insol. in petroleum ether, crystals, m. 35.5°, liquid, *d*<sub>4</sub> 1.1159. B gives a violet color with FeCl<sub>3</sub> and reduces NH<sub>4</sub>-AgNO<sub>3</sub>, forms a cryst. bisulphite compd. *Semicarbazone* of B, m. 213°. The *nitrile of p-methoxybenzyl-lactic acid* (C) was made by treating A with KCN in 60% yield as an oil which can be distd. only under reduced pressure. C was converted to the *amide* by the usual method, giving a white powder, recrystd. from alc., silky needles, m. 179°, insol. in H<sub>2</sub>O, slightly sol. in Et<sub>2</sub>O, sol. in alc., especially hot, and in CS<sub>2</sub>. By complete hydrolysis with HCl C gave the corresponding acid, MeOC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>C(OH)MeCO<sub>2</sub>H, colorless silky needles from alc., m. 84°, easily sol. in alc. and CS<sub>2</sub>. Isobutenylanisole (D) was made (1) by treating A with MeMgI; (2) by the action of Me<sub>2</sub>CHCHO on MeOC<sub>6</sub>H<sub>4</sub>MgBr. D is a colorless liquid with a feeble aromatic odor, *d*. 1.0089. It gives a dibromide and decolorizes KMnO<sub>4</sub>. D is oxidized by KMnO<sub>4</sub> to anisic acid, m. 180°. *p*-Methoxyphenyl-1-methyl-2-propane was prepd. by reducing the hydrocarbon with Na in abs. alc. as a colorless liquid, *b*<sub>16</sub> 123-25°, *d*. 0.9887. PhCH<sub>2</sub>MgCl with A gave *p*-methoxyphenyl-1-methyl-2-phenyl-3-propanol (E). The dehydration of E with Ac<sub>2</sub>O gave 1-*p*-methoxyphenyl-2-methyl-3-phenyl-1,2-propene (F), as a colorless liquid, *b*<sub>17</sub> 206°, *d*. 1.0551. It forms a dibromide and decolorizes KMnO<sub>4</sub>. Oxidation of F with CrO<sub>3</sub> gave anisic acid. R. CHESTER ROBERTS

**Two  $\alpha,\alpha,\beta,\beta$ -substituted propiophenones, and their products of decomposition by means of sodamide.** MME. RAMART AND G. ALBESCO. *Compt. rend.* **174**, 1289-91 (1922).—Sodamide is effective in promoting both the alkylation of such compds. as Ph<sub>2</sub>CHCH<sub>2</sub>COPh by means of alkyl iodide in PhH, and the splitting of the alkylated product according to the following reactions, both of which take place, and to about the same extent: (1) "Ph<sub>2</sub>CHCHR<sub>2</sub>COPh + NaNH<sub>2</sub> → Ph<sub>2</sub>CHCHR<sub>2</sub>CONH<sub>2</sub> + PhH," and, (2) "Ph<sub>2</sub>CHCHR<sub>2</sub>COPh + NaNH<sub>2</sub> → Ph<sub>2</sub>CHCHR<sub>2</sub> + PhCONH<sub>2</sub>"; (1) is a general reaction for the prepn. of  $\alpha,\alpha$ -dialkyl- $\beta,\beta$ -substituted propionic acids (cf. Nef, *Am. Chem. J.* **33**, 89). The substituted ketones are prepd. by first treating PhCH:CHCOPh with RMgX, giving PhRCHCH<sub>2</sub>COPh (cf. *Am. Chem. J.* **31**, 642; **33**, 21; *Compt. rend.* **142**, 971 (1906)), and alkylating the product; Ph<sub>2</sub>CHCH<sub>2</sub>COPh is dimethylated in 2 steps; the mono-Me deriv. m. 103°, and is identical with the product obtained by the action of PhMgBr on PhCH:CMcCOPh. Ph<sub>2</sub>CHCMcCOPh, prepd. from the mono-Me deriv. by further methylation in the same way, forms colorless prisms, m. 90°, and when treated in xylene with NaNH<sub>2</sub>, gives Ph<sub>2</sub>CHCHMc<sub>2</sub>, colorless liquid, *b*<sub>13</sub> 145°; also BzNH<sub>2</sub> and BzOH; Ph<sub>2</sub>CHCMc<sub>2</sub>CO<sub>2</sub>H, m. 134°; Ph<sub>2</sub>CHCMc<sub>2</sub>CONH<sub>2</sub>, m. 122°; and (Ph<sub>2</sub>CH)<sub>2</sub>. The di-ethylation of PhEtCHCH<sub>2</sub>COPh is carried out also in 2 stages, by means of EtBr in the presence of NaNH<sub>2</sub> and PhH; the products of the reaction are: (1) PhEtCHCHEtCOPh, m. 68°, fine needles, identical with the condensation product of PhCH:CH<sub>2</sub>COPh and EtMgBr; and (2) PhEtCHCHEt<sub>2</sub>COPh, an oil *b*<sub>10</sub> 180°, probably not quite pure, which on treatment with excess NaNH<sub>2</sub> in PhMe gives PhEtCHCHEt<sub>2</sub>, *b*<sub>10</sub> 205°; BzOH; and PhEtCHCHEt<sub>2</sub>CO<sub>2</sub>H, m. 82°, from Et<sub>2</sub>O-petr. ether. A. R. ALBRIGHT

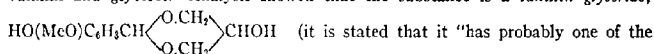
**Amino alcohols. Homologs of novocaine.** E. FOURNEAU AND J. PUYAL. *Bull. soc. chim.* **31**, 424-35 (1922).—Unsatd. hydrocarbons, prepd. by passing vapors of the corresponding alcs. over an infusorial earth prepn. as a catalyst, and absorbed in 2% Br water give the corresponding bromohydrins. 3-Bromo-2-butanol, *b*. 154°, *b*<sub>4</sub> 63°, *d*. 1.5016, from BuOH; 3-chloro-2-butanol, *b*. 138-40°, by passing butylene into aq. HOCl contg. 2.2% Cl. Both of these on treatment with dry NaOH gave good yields



of sym. dimethylethylene oxide. *1-Bromo-2-methyl-2-butanol*,  $b_{18}$  67°, d. 1.42, from amylene (b. 33-5°) and Br water. Dialkylamino alcs. were prepd. from the bromohydrins by heating for 6 hrs. at 125° in sealed tubes with a PhH soln. of the dialkylamine. *Dimethylamino-2-propanol*,  $b_{40}$  45°; yield, 6 g. from 12 g. bromohydrin. *Diethylamino-2-propanol* b. 157°; *3-dimethylamino-2-butanol* b. 145°,  $b_{18}$  53°; *3-diethylamino-2-butanol* b. 167-72°,  $b_{18}$  74°; *1-dimethylamino-2-methyl-2-butanol* b. 144-6°,  $b_{18}$  53°. Treatment of these  $NH_2$  alcs. with  $p-O_2NC_6H_4COCl$  in PhH gives the corresponding *p*-nitrobenzoic ester hydrochlorides. Reduction of the latter with Sn and HCl and subsequent removal of Sn by  $H_2S$  gives the hydrochlorides of the *p*-aminobenzoates, which are homologs of procaine. *Dimethylaminoisopropyl p-nitrobenzoate hydrochloride* m. 198°; yield, 7 g. from 3 g. of the  $NH_2$  alc. *Diethylaminoisopropyl p-nitrobenzoate hydrochloride* (A), needles m. 187°; *diethylaminoisopropyl p-aminobenzoate hydrochloride* (methylnovocaine), m. 150-2°, prepd. by reduction of A with Sn and HCl, is a stronger anesthetic than novocaine. *3-Diethylamino-2-butanol p-nitrobenzoate hydrochloride* (B), m. 148°, has a very bitter taste and is anesthetic to the tongue. *3-Diethylamino-2-butanol p-aminobenzoate hydrochloride* (dimethylnovocaine), m. 172°, by reduction of B with Sn and HCl in the presence of  $PtCl_4$ , has an anesthetic effect much more intense than that of novocaine. *1-Dimethylamino-2-methyl-2-butanol p-nitrobenzoate hydrochloride* (C), needles, m. 184°, has a very bitter taste, is difficultly sol. in  $Me_2CO$  and less sol. in  $H_2O$  and  $EtOH$  than stovaine. *1-Dimethylamino-2-methyl-2-butanol p-aminobenzoate hydrochloride* (aminostovaine) (D), m. 73°, by reduction of C with Sn and HCl, is very sol. in PhH and  $EtOH$ , hygroscopic and difficult to cryst. *Hydriodide*, m. 159°, which seps. on treating a soln. of D with excess of KI, is a very powerful anesthetic. The *cinnamate hydrochloride*, m. 203°, is easily crystd. A comparison of the derivs. from the pentene obtained by catalytic dehydration of iso-AmOH with those obtained from Kahlbaum's "pental" shows that the catalytic amylene contains about 70% and pental about 20% of methylethylethylene.

A. W. DOX

**Vanillin glyceride.** F. D. DOUGL. *J. Am. Chem. Soc.* **44**, 1405-7 (1922).—A flavoring mixt. consisting essentially of alc., glycerol and vanillin deposited an almost odorless microcryst. powder sepg. from alc. in plates easily sol. in 0.5 *N* KOH, reprecip. by acids and slowly hydrolyzed by heating with  $H_2O$ , much more rapidly by acids, into vanillin and glycerol. Analysis showed that the substance is a *vanillin glyceride*,



following two structural formulas," but the 2 formulas given are identical. ABSTR.). Its formation from the components can be greatly accelerated by the addition of mineral acids but the latter are a very disturbing factor in the isolation of the product; by working in the cold and as rapidly as possible the crystals can be freed from the mother liquor before much hydrolysis occurs; any trace of acid left causes complete decompn. of the compd. in a short time. It m. about 160-2°.

C. A. R.

**Action of potassium iodide and iodate on some hydroxy acids.** SRI KRISHNA AND F. G. POPP. *J. Chem. Soc.* **121**, 798-800 (1922).—*o*- and *p*- $C_6H_4(OH)CO_2H$  in  $H_2O$ , added in small quantities to aq. KI and  $KIO_3$  at 50°, form  $C_6H_4(OH)I_3$ , the  $CO_2H$  group being eliminated. 3- and 5- $O_2NC_6H_3(OH)CO_2H$  gave 2,5,6-triido-3-nitrophenol (?), shining yellow plates, m. 148°. The triido derivative from the 3,5-( $O_2N$ ) $_2$  $C_6H_2(OH)CO_2H$  forms glistening plates, m. 165°. In the case of *o*- $H_2NC_6H_4CO_2H$ , and its Ac deriv., direct substitution by I appears to take place without elimination of the  $CO_2H$  group. The product in the 1st instance is ( $\beta$ )-3-iodo-2-aminobenzoic acid, m. 208-9°, and in the 2nd an iodoacetylanthranilic acid, shining plates, m. 175°. The action of KI and  $KIO_3$  is much more rapid than that of the corresponding Cl or Br derivs.

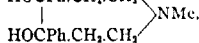
C. J. WESS

**Reduction of substituted salicylic acids.** HUGO WEIL AND KARL BRIMMER. *Ber. 55B*, 301–5 (1922).—From 55 g. sulfosalicylic acid in  $H_2O$  (neutralized with 10.6 g. soda) treated with 160 g. of 40%  $NaHSO_3$  (neutralized to litmus with  $NaOH$ ) and 60 g.  $H_2BO_3$ , dild. to 2:1. and slowly treated with 450 g. of 3.5%  $Na-Hg$  with cautious addition of  $HCl$  to keep the soln. always faintly acid, then boiled 15 min. with dil. acid to destroy the bisulfite compd., neutralized to Congo with  $NaOAc$  and treated with  $PhNH_2$ , are obtained thick yellow flocks of the compd.  $HO_2SC_6H_4(OH)CH:NPh$  (yield, 57%), balling to yellow leaflets on heating, which, decompd. in soda soln. with steam, yield  $PhNH_2$  and sodium sulfosalicylaldehyde,  $NaO_2SC_6H_4(OH)CHO$ . 1.5  $H_2O$ ; 12.5 g. of the aldehyde heated 24 hrs. at  $110^\circ$  with 5 g.  $H_2SO_4$  and 14 g.  $PhNMe_2$ , made alk. with  $NaOH$ , distd. with steam and made faintly acid gives 13 g. of a leuco salt,  $C_{23}H_{29}ON_2SO_3Na \cdot 2H_2O$ , silvery leaflets yielding on oxidation a blue-green dye. Disodium disulfosalicylaldehyde, crystals with 2.5  $H_2O$ , is obtained in 75% yield by treating the sulfonamide mixt. in a little  $H_2O$  with  $NaCl$ ; 17.1 g. reduced as above and treated with a large excess of  $p-MeC_6H_4NH_2$  gives the reddish cryst. salt  $MeC_6H_4N:CHC_6H_4(OH)(SO_3H.NH_2C_6H_4Me)_2$ , which on decompn. with  $K_2CO_3$  yields 22% of dipotassium salicylaldehydedisulfonate, crystals with 2  $H_2O$ ; barium salt, granular crystals with 2.5  $H_2O$ . The  $K$  salt (1.9 g.) allowed to stand a short time with 0.8 g.  $p-MeC_6H_4NH_2 \cdot HCl$  in a little  $H_2O$  gives the yellow cryst. salt  $C_{14}H_{11}ON(SO_3K)_2 \cdot H_2O$ ; with 2 g.  $MeC_6H_4NH_2$  in  $AcOH$  is obtained the orange cryst. salt  $C_{14}H_{11}ON(SO_3H.NH_2C_6H_4Me)_2$ . The aldehyde (2 g.) in  $H_2O$  with 0.6 g.  $PhNHNH_2$  in  $AcOH$  and subsequent treatment with  $BaCl_2$  gives the salt  $C_{13}H_{10}ON_2(SO_3)_2Ba$  as a yellow slimy mass becoming cryst. with time. 1-Hydroxybenzene-2,6-dialdehyde, obtained in 22% yield by reduction as above of 2,3-HO(OHC)- $C_6H_2CO_2H$ , odorless hair-like needles, volatile with steam, m.  $125^\circ$ ; diphenylhydrazone, yellow crystals from alc. 1-Hydroxybenzene-2,4-dialdehyde, obtained in 40% yield from 2,5-HO(OHC)- $C_6H_2CO_2H$ , fine yellowish needles from  $H_2O$ , practically non-volatile with steam, m.  $113^\circ$ ; diphenylhydrazone, yellow cryst. ppt. from alc.; heated 20 hrs. at  $110^\circ$  with  $H_2SO_4$  and  $PhNMe_2$ , treated with excess of  $NaOH$  and distd. with steam, the aldehyde gives a bluish substance which in  $HCl$  with  $ZnCl_2$  forms a non-cryst. double salt; this, dissolved in  $H_2O$  and poured into hot dil.  $NH_4OH$ , gives the compound  $C_{10}H_8ON_4$ , yielding with  $PbO_2$  a blue dye. C. A. R.

**3-Hydroxy-*o*-toluic acid.** Y. ASHINA AND Y. KONDO. *J. Pharm. Soc. Japan No. 482*, 264–71 (1922).—A. and his coworkers (*C. A.* 10, 1523, 1524), obtained a cresotic acid by alk. fusion of hydrangenols and phylodulcins isolated from *Hydrangen hortensia* Max, and identified it as 3-hydroxy-*o*-toluic acid (A), identical with the product obtained by A. and Furukawa (*C. A.* 12, 473) by alk. fusion of 4-bromo-*o*-toluic acid. Another method of prepn. of A is reported here. By the method of Gabriel and Thieme (*Ann.* 228, 240): *o*-acetotoluidide  $\rightarrow$  3-nitro-*o*-toluidine  $\rightarrow$  3-nitro-*o*-tolunitrile  $\rightarrow$  3-nitro-*o*-toluic acid  $\rightarrow$  3-amino-*o*-toluic acid, then 1 g. of the  $NH_2$  acid in an equal vol. of 0.5  $N$   $HCl$  is diazotized in ice with 0.51 g. of  $NaNO_2$  (90%). When the mixt. is heated on the water bath to drive off  $N$ , resinous matter is produced.  $HCl$  is added to the cooled soln., then  $NaCl$ , and it is extd. with ether. 0.8 g. of a cryst. compd. is obtained which when recrystd. from hot  $H_2O$  gave 2 g. of A. The sublimed product m.  $169-70^\circ$ . Since this method is tedious up to the prepn. of the  $NH_2$  acid, the original method of A. and F. is recommended for the prepn. of A. S. T.

**Synthesis of  $\beta$ -keto bases from acetophenone, formaldehyde and amine salts.** C. MANNICH AND G. HEILNER. *Ber. 55B*, 356–65 (1922); cf. *C. A.* 15, 861.—From 40 g.  $PhCOMe$ , 10 g. paraform and 27.5 g.  $NHMe_2 \cdot HCl$  boiled in alc. is obtained 42 g. of the hydrochloride (A), leaflets from alc., needles from  $Me_2CO$ , m.  $156^\circ$ , of  $\omega$ -dimethylamino-propiofenone,  $b_{14}$   $110-2^\circ$ ; oxime, tables from dil. alc., m.  $108^\circ$ . A (2.2 g.) decolorizes 8.8 g.  $KMnO_4$ , yielding  $CO_2$ ,  $BzOH$  and  $NHMe_2$ . Steam decomp. A into  $PhCOCH:CH_2$  and  $NHMe_2 \cdot HCl$ . Hydrogenation of A in  $H_2O$  with palladinized charcoal generally

gave quant. the *hydrochloride*, leaflets from  $\text{Me}_2\text{CO}$ , m.  $135-6^\circ$ , of *1-phenyl-3-dimethyl-amino-1-propanol* (B), oil of a basic odor; *benzoate*,  $b_{14}$   $130-60^\circ$  (*hydrochloride*, m.  $170^\circ$ ). In one case the reduction of A proceeded beyond the alc. stage, giving a mixt. of bases  $b_{14}$   $80-130^\circ$ , sepd. by benzylation by the Schotten-Baumann method into 2 fractions  $b_{14}$   $80-100^\circ$  and  $100-80^\circ$ ; distn. of the 1st fraction under atm. pressure yielded  $\text{PhCH}_2\text{-CH}_2\text{CH}_2\text{NMe}_2$ , b.  $215-20^\circ$  (methiodide, m.  $175.5^\circ$ ; picrate, m.  $103^\circ$ ; chloroplatinate, m.  $151^\circ$ ). A and activated Al in  $\text{Et}_2\text{O}$  gently warmed several hrs. with gradual addition of  $\text{H}_2\text{O}$  yielded, besides a little B, chiefly 2 isomeric *1,6-bis*[dimethylamino]-3,4-diphenyl-hexanedials (*dl*- and *meso*-forms):  $\alpha$ , m.  $146^\circ$ , and  $\beta$ , sinters about  $100^\circ$ , m.  $107^\circ$ .  $\alpha, \alpha'$ -Bis[phenylacetylmethyl]methylamine (methylbis- $[\beta$ -benzoylethyl]amine) (C), rodlets or needles, m.  $142^\circ$ , is obtained as the *hydrochloride* (20.5 g.), needles from alc., m.  $162^\circ$ , from 48 g.  $\text{PhCOMe}$ , 12 g. paraform and 14.8 g.  $\text{NH}_2\text{Me.HCl}$ ; the mother liquor contains a small amt. of  $\omega$ -methylaminopropiophenone *hydrochloride* (D); best prepd. by distg. the preceding salt with steam, whereby  $\text{PhCOCH:CH}_2$  is also formed; D seps. from  $\text{Me}_2\text{CO}$  in leaflets, m.  $139-41^\circ$ ; it can also be obtained in 7 g. yield from 12 g.  $\text{PhCOMe}$ , 7 g.  $\text{NH}_2\text{Me.HCl}$  and 3 g. paraform boiled a short time in 15 cc. alc., filtered, freed from alc. by evapn., stirred with  $\text{Et}_2\text{O}$  (which removes 5.8 g. unchanged  $\text{PhCOMe}$ ) and distd. with steam. C (10 g.), reduced in  $\text{Et}_2\text{O}$  with activated Al, gives 1.2 g. of a compd. sepg. from alc. in leaflets, m.  $205^\circ$ , and 2 g. of an isomer, fine needles from  $\text{Me}_2\text{CO}$ , sinters about  $170^\circ$ , m. around  $180^\circ$ ; the compds. are probably *dl*- and *meso*-forms of the cyclic *pinacol*  $\text{HOCHPh.CH}_2\text{CH}_2\text{NMe}$ .



C. A. R.

**Transformations of some secondary  $\beta$ -keto bases.** C. MANNICH AND G. HEILNER. *Ber.* 55B, 385-74(1922); cf. preceding abstr.— $\text{PhCOCH}_2\text{CH}_2\text{CH}_2\text{NHMe.HCl}$  (A) in concd. soln. strongly acidified with HCl, treated in ice with an excess of concd.  $\text{NaNO}_2$  and warmed slightly, gives 90% of  $\omega$ -[nitrosomethylamino]propiophenone, prismatic columns or needles from petr. ether, m.  $66^\circ$ ; 9 g. in  $\text{MeOH-AcOH}$  with 45 g. Zn dust gives 3-3.5 g. of a *hydrochloride*, needles from  $\text{Me}_2\text{CO}$ , m.  $162^\circ$ , of *1-methyl-3-phenyl-pyrazoline*, leaflets with fatty luster and characteristic odor from petr. ether, m.  $37^\circ$ . *asym*-[Phenacylomethyl]methylurea (1.8 g. from 1 g.  $\text{KCNO}$  and 2 g. A gently warmed in concd. aq. soln.), needles from  $\text{C}_6\text{H}_6$ , m.  $123-4^\circ$ , decomps. in boiling  $\text{H}_2\text{O}$  with evolution of the odor of  $\text{PhCOCH:CH}_2$ , insol. in cold dil. mineral acids but easily sol. in alkalis and therefore probably can exist also in the enol form  $\text{PhC(OH):CHCH}_2\text{NMeCO.NH}_2$ ; dissolved in warm  $\text{H}_2\text{O}$ , quickly cooled, treated at once (before crystn. begins) with a mineral acid (about 1 cc. concd. HCl per 3 g. urea) and immediately cooled strongly, it gives almost quant. *1-methyl-4-phenyl-2-keto-1,2,5,6-tetrahydropyrimidine*, spears from alc., m.  $152-4^\circ$ ; when 10 g. of this compd. in 70 cc.  $\text{H}_2\text{O}$  is boiled with 50 cc. 2 N  $\text{H}_2\text{SO}_4$  until the ppt. redissolves and then made faintly alk. to phenolphthalein with  $\text{Ba(OH)}_2$  there seps. with the  $\text{BaSO}_4$  3.5 g. *1-methyl-4-phenyl-2-keto-1,2-dihydropyrimidine*, felted needles from alc., m.  $217^\circ$ , while the filtrate contains the *hexahydro compound* (together with about 0.5 g. of the dihydro compd.), stout spears or prisms from  $\text{C}_6\text{H}_6$ , petr. ether, m.  $115-6^\circ$ , also obtained in 0.8 g. yield from 1 g. of the dihydro compd. in dil. alc.-HCl with H and palladinized charcoal, or from the tetrahydro compd. in the same way. The dihydro compd. in AcOH with Br gives the *5,6-dibromide* (B), light yellow leaflets from AcOH, m.  $260^\circ$  (decompn.), loses all of its Br to alc. KOH. The tetrahydro compd. with 2 mols. Br in AcOH gives HBr and a white *tribromo derivative*,  $\text{C}_{11}\text{H}_{10}\text{ON}_2\text{Br}_3$ , decomps.  $260^\circ$ , easily loses HBr, dissolves in cold alkalis with yellow color, gives B with boiling AcOH. The Br probably first oxidizes the 5- and 6-H atoms, forming a dihydro deriv., which then adds 2 atoms of Br and 1 mol. of the HBr formed, the tri-Br compd. having the structure  $\text{PhCBr.CHBr.CHBr.NMe.CO.NH}$ . B on

shaking with much  $H_2O$  slowly loses 1 mol.  $HBr$ , forming *1-methyl-4-phenyl-2-keto-6-(or 5)-bromo-1,2-dihydropyrimidine* (more easily obtained from **B** in a little  $H_2O$  with  $NaHCO_3$ ), fine needles from alc., m.  $177^\circ$ ; this in  $AcOH$  with 1 mol.  $Br$  gives about 75% of an orange cryst. substance which smells intensely of  $Br$ ; a sample kept some hrs. in a desiccator contained 61.6%  $Br$ , which corresponds to a tetrabromide; boiled or heated alone, in  $AcOH$  it gives **B**. Antipyrine (3.8 g.) and 4 g. **A** in 4 cc.  $H_2O$  allowed to stand 3 days in a closed vessel with 2 cc. of 30%  $HCHO$  give the *hydrochloride*, crystals from  $Me_2CO-EtOH$ , m.  $164^\circ$ , of  $\alpha$ -[phenacylomethyl]- $\alpha'$ -[antipyrino-4-methyl]methylamine,  $PhCOCH_2CH_2NMeCH_2C:CMc.NMe.NPh.CO$ , fine slender needles or spars from

$C_6H_6$ -petr. ether, m.  $86^\circ$ .

C. A. R.

**The iodohydrin derivative of allylbenzene and its transformations.** M. PORCHER. *Bull. soc. chim.* 31, 334-40 (1922).—It has been shown by P. and Tiffeneau (*Bull. soc. chim.* 31, 324 (1922)) that in the compds.  $PhCH_2C(OH)RCHIR'$ , if  $R$  is part of a cyclic group the  $PhCH_2$ -radical migrates in preference to  $R$ . A study is made to det. if the same reaction occurs when  $R$  and  $R'$  are  $H$  atoms.  $PhCH_2CH(OH)CH_2I$  (**A**) in  $Et_2O$  shaken with  $AgNO_3$  soln., decanted, washed with  $Et_2O$ , let stand 2 hrs., the  $Et_2O$  soln. washed with  $H_2O$ , distd. *in vacuo* at room temp., the oil made alk. with  $K_2CO_3$ , steam distd., extd. with  $Et_2O$ , dried, evapd., the residue treated with  $H_2NCONHNH_2.HCl$  and  $NaOAc$ , let stand 1 day, yields from hot  $EtOH$  the semicarbazone of  $PhCH_2COMe$ . The mother liquor dild. with  $H_2O$  and steam distd. yields  $PhCH_2CHCH_2O$  (**B**). The

residue from the steam distn. satd. with dry  $K_2CO_3$ , extd. with  $Et_2O$ , evapd., the oil distd. *in vacuo*, yields  $PhCH_2CH(OH)CH_2OH$ . **A** shaken with aq.  $KOH$ , kept at  $100^\circ$  for 2 hrs., satd. with  $CO_2$ ,  $K_2CO_3$  added, extd. with  $Et_2O$ , yields  $PhCH(OH)CH_2OH$ . **B** treated with concd.  $HI$  forms a mixt. of  $PhCH_2CH(OH)CH_2I$  and  $PhCH_2CHICH_2OH$ .  $PhCH_2CHBrCH_2Br$  added slowly to alc.  $KOH$ , cooled by stream of water, filtered,  $CO_2$  passed through, the alc. distd. *in vacuo* at a low temp., the residue extd. with  $Et_2O$ , the ext. yields on rectification  $PhCH_2CH:CHBr$  and a liquid  $b$ ,  $228-9^\circ$ ,  $d_4$  1.163, probably the corresponding vinyl ether.  $PhCH_2CH:CHBr$  treated in  $Et_2O$  with  $Mg$ ,  $CO_2$  passed through, ice added, acidulated with dil.  $H_2SO_4$ , extd. with  $Et_2O$ , the ext. washed with aq.  $Na_2CO_3$ , dried, evapd., the residue distd. *in vacuo*, then at ordinary pressure yields  $CH_2:CHCH_2Ph$  and  $PhCH_2C:CH$ . The alk. soln. washed with  $Et_2O$ , acidulated, extd. with  $Et_2O$ , yields  $PhCH_2CH:CHCO_2H$ .

C. C. DAVIS

**Semipinacolic transformation in the benzylcyclohexene series; migration of the benzyl radical.** M. TIFFENEAU AND M. PORCHER. *Bull. soc. chim.* 31, 324-34 (1922).—The semipinacolic transposition of iodohydrin derivs. (cf. C. A. 16, 1232) is applied to benzyl derivs. of cyclic compds. 30 g. of benzylcyclohexanol (**A**) distd. *in vacuo* with  $H_2SO_4$ , the distillate extd. with  $Et_2O$ , washed with  $H_2O$ , dried with  $Na_2SO_4$  and redistd. *in vacuo* yields 24 g. of *1-benzyl-1,2-cyclohexene* (**B**), oil,  $b_D$   $132-4^\circ$ ,  $d_4$  0.9802. It is not isomerized by  $NaOH$ . With cold  $KMnO_4$  it forms  $BzOH$  and a glycol which is stereoisomeric with benzylcyclohexanediol. *Dibromide*, liquid. **B** treated with  $HgO$  and  $I$ , washed with concd.  $KI$  contg.  $NaHSO_3$ , evapd. *in vacuo*, yields *1-benzyl-2-iodo-1-cyclohexanol* (**C**), yellowish oil, turning brown with liberation of  $I$ , reacts with  $NaOAc$  in  $HOAc$  to form a compd. which on sapon. gives *1-benzyl-1,2-cyclohexanediol*. **C** in  $Et_2O$  shaken with aq.  $AgNO_3$ , let stand 1 day, decanted, the  $Et_2O$  soln. washed with  $H_2O$ , dried with  $Na_2SO_4$  and evapd. *in vacuo*, the oil made alk. with  $K_2CO_3$ , steam distd., extd. with  $Et_2O$ , dried with  $Na_2SO_4$  and distd. yields an oil,  $b_D$   $130-65^\circ$ , contg. a mixt. Fractional distn. yields 3 compds., **A**, **B**, and *1-benzyl-2-cyclohexanone* (**D**), oil,  $b_D$   $165-6^\circ$ ,  $d_4$  1.0733. It was purified by means of its *semicarbazone*, fine needles, m.  $166-7^\circ$ . **D** with cold  $KMnO_4$  forms  $BzOH$  and the same glycol obtained from **B**. It does not react with  $NaHSO_3$  or with  $BzH$ . **D** prepd. by heating cyclohexanone,  $NaNH_2$  and

BzCl in  $C_6H_6$ , adding  $H_2O$  and treating in the usual way yields a compd.  $b_p$  160–5°,  $d_4$  1.0508, with a semicarbazone m. 166–7°. The residue from the steam distn., extd. with  $Et_2O$ , dried with  $Na_2SO_4$  and distd. yields *1-benzyl-1,2-cyclohexanedial* (E), large needles from petr. ether, m. 96–7°. E heated with dil.  $H_2SO_4$  forms D. C heated with dil. aq. KOH for 6 hrs. with shaking forms a clear yellow oil. This steam-distd., extd. with  $Et_2O$ , dried, and distd. *in vacuo* yields *1-benzyl-2-hydroxy-1-cyclohexanol* (F), liquid,  $b_p$  150°,  $d_4$  1.0428, gives no semicarbazone. F heated with dil.  $H_2SO_4$  for 2 hrs., extd. with  $Et_2O$ , dried, distd. and purified by formation of its semicarbazone yields D. 1,4-Methylbenzyl-4-cyclohexanol distd. *in vacuo* with concd.  $H_2SO_4$ , extd. with  $Et_2O$  and redistd., yields *1,4-methylbenzyl-3,4-cyclohexene*, oil  $b_p$  160–5° (G). *1,4-Methylbenzyl-3-iodo-4-cyclohexanol* (H) obtained from G in a manner analogous to C and B, sirupy liquid, decomp. on distn. and slowly in the cold with liberation of I. Treated with  $AgNO_3$  as in the preceding instance, only 3–4% of the compd. reacted to liberate HI, and no evidence of migration of the atoms was obtained. C. C. DAVIS

**Use of the oxides of platinum for the catalytic reduction of organic compounds.** I. V. VOORHEES with ROGER ADAMS. *J. Am. Chem. Soc.* **44**, 1397–405(1922).—Since it seems that the O, which must always be present in Pt black if the latter is to be an active catalyst, is present in the form of an oxide of Pt, the oxides of Pt are being studied with respect to their catalytic activity. Fusion of  $H_2PtCl_6$  with  $NaNO_3$  gives an oxide which has proved to be an excellent catalyst; various types of org. compds. (phenols,  $C_6H_5N$  derivs., aromatic and aliphatic aldehydes and heterocyclic compds.) have been reduced by means of it, the speed of reduction being greater than with ordinary Pt black. C. A. R.

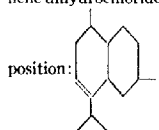
**New preparation of cyclomethylamines.** ALPHONSE MAILHE. *Bull. soc. chim.* **31**, 340–4(1922).—By a method already described (cf. *C. A.* **15**, 1498) it was attempted to prep. cyclomethylamines by hydrogenation of cyclomethylketazines and ketones. Direct hydrogenation of the hydrazones and ketazines of cyclohexanone and of methylcyclohexanones was effected with great ease by finely divided Ni at 180°. High yields were obtained of primary cyclomethylamines, cyclohexylamine and methylcyclohexylamines, together with small proportions of secondary amines. All hydrogenations were carried out with the same Ni. Without intermediate treatment it retained its activity throughout. In this way there were prepd. from a mixt. of the hydrazone and ketazine of cyclohexanone, a mixt. of cyclohexylamine and dicyclohexylamine; from a mixt. of the hydrazone and ketazine of *o*-methylcyclohexanone, a mixt. of (1) *o*-methylcyclohexylamine (A), liquid,  $b_p$  150°,  $d_4^{25}$  0.8836, with bitter taste, strongly alk. to litmus, reddens phenolphthalein, decomp. in the air very rapidly; *hydrochloride*, m. 280°, insol. in  $Et_2O$ , gives the carbylamine reactions; and (2) *di-o-methylcyclohexylamine*, oil,  $b_p$  268–70°, sol. in org. solvents, very alk. to litmus, forms ppts. with Cu and Ag salts; *hydrochloride*, m. 226°. *m*-Cyclohexanone reduced by H forms only *m*-methylcyclohexylamine,  $b_p$  152°,  $d_4^{25}$  0.8956, alk. to litmus, decomp. in the air less rapidly than A, gives the carbylamine reaction, forms  $OC(NHC_4H_9Me)NHPh$  with  $PhNCO$  in petr. ether. A mixt. of the hydrazone and ketazine of *p*-methylcyclohexanone reduced by H forms a mixt. of (1) *p*-methylcyclohexylamine (B),  $b_p$  153°,  $d_4^{25}$  0.9057, strongly alk., decomp. rapidly in the air; *hydrochloride*, brilliant plates, m. 245° (decompn.); and (2) *di-p-methylcyclohexylamine* (C),  $b_p$  273°, very alk. to litmus, forms ppts. with Cu and Ag salts; *hydrochloride*, m. 198°. The yield of B was greater than C. C. C. DAVIS

**Higher terpene derivatives. II. Abietic acid.** L. RUZICKA and J. MEYER. *Helvetica Chim. Acta* **5**, 315–44(1922); cf. *C. A.* **15**, 3476.—Abietic acid (A) is the chief constituent of American colophonium and has been the object of numerous investigations. Its formula is  $C_{20}H_{30}O_2$  and some insight into the structure has been gained by

its dehydrogenation to *relene*,  $C_{14}H_{18}$ , by Vesterberg (*Ber.* 36, 4200(1903)) and the identification of the latter as *1-methyl-7-isopropylphenanthrene* by the works of Bamberger and Hooker (*Ann.* 229, 102), Fortner (*Monatsh.* 25, 452), Lux (*Monatsh.* 29, 763), and Bucher (*J. Am. Chem. Soc.* 32, 374). There remains however to be fixed the position of the 2 double bonds and of the Me and  $CO_2H$  groups which were eliminated in the above dehydrogenation to retene. In the light of present knowledge A is a methyldecahydroretene-carboxylic acid and belongs to the *diterpene series*. In the extn. of A from American colophonium different methods have yielded the product with widely different m. p. and  $[\alpha]_D$ . R. and M. have isolated it by distn. in high vacuum (1 mm.), obtaining an acid, m. 158°, with  $[\alpha]_D -68^\circ$  (alc.). This checks well with the results of Maly, Fluchtiger, and Tschirch and Studer, all of whom used more gentle methods of extn. On the other hand Levy, by distn. at 12–15 mm. obtained a high melting acid, m. 182°; and Johansson, by distn. with superheated steam, obtained an acid m. 168–173°,  $[\alpha]_D 28^\circ$  (alc.). R. and M. then found that at 2 mm. they obtained an acid m. 160°,  $[\alpha]_D -61^\circ$  (alc.), and furthermore they found that by heating the acid (m. 158°) at 300° for some time, an acid m. 170–2°,  $[\alpha]_D 46^\circ$  (alc.), was obtained. It seems clear then that *the acid m. 158° is the one actually present in the colophonium* and the higher melting acids are formed from it by the action of heat. Analysis of various fractions of the vacuum distn. gave always  $C_{20}H_{30}O_2$  showing that the American colophonium consists almost entirely of isomeric resin acids. Levy found that in distg. at 12 mm.  $CO_2$  and *abietene* were formed to some extent. These did not appear at 1 mm., nor did the acid m. 158° give any noticeable amt. on distg. at 12 mm., unless it were previously heated at 300° for some time. These products of the distn. at 12 mm. appear to result from the decompn. of the higher melting acids. The isomerizing action of alkalis on A was found practically nil. Glacial HOAc causes only slight changes. A strong HOAc-HCl mixt. gave at 100° an acid m. 176°,  $[\alpha]_D -34^\circ$  (alc.). With regard to the nature of the unsatn. of A, Wienhaus (*Z. angew. Chem.* 1921, 254) has proposed a tetracyclic structure with one double bond, based chiefly on his inability to obtain from A either a tetrahydroxy deriv. with  $KMnO_4$ , or a tetrahydro deriv. by catalytic reduction. R. and M. have found however that although catalytic reduction in EtOH gives only a dihydro deriv. m. 167° there is readily obtained in EtOAc, AmOAc, or HOAc the tetrahydro deriv. m. 158–165°. This action together with the results obtained for the mol. refractivity, and by ozonification lead R. and M. to support the 2 double bond idea. The various isomerized acids reacted essentially the same towards catalytic reduction and ozonification, indicating that probably the only differences are of optical and geometrical isomerism. R. and M. intend to carry out a similar study on the *pimaric acid* of the French colophonium.

**III. The naphthalene hydrocarbons cadalene and eudalene, two aromatic sources of the sesquiterpenes.** L. RUZICKA, J. MEYER and M. MINGAZZINI. *Ibid* 345–68.—Since the hydrocarbons  $C_{14}H_{14}$  and the tertiary alcs.  $C_{14}H_{16}O$  are the chief representatives of the natural sesquiterpenes they can be classified somewhat satisfactorily upon the basis of the mol. refractivity into 4 groups; viz., (1) *tricyclic*, d. 0.935–0.91,  $M_D$  64.4; (2) *dicyclic*, d. 0.92–0.90,  $M_D$  66.1; (3) *monocyclic*, d. 0.873,  $M_D$  67.8; and (4) *aliphatic*, d. 0.84,  $M_D$  69.5. Semmler (*Ber.* 46, 1817; 47, 2557) has further subdivided on the basis of density the tricyclic sesquiterpenes into (a) the *cedrene* family, d. 0.935, and the (b)  *$\alpha$ -santalene* family, d. 0.91, and the dicyclic sesquiterpenes into (a) the *cadimene* family, d. 0.917, and (b) the *caryophyllene* family, d. 0.90. *Farnesol*, an aliphatic alc., is the only member of the whole sesquiterpene series whose exact constitution is known (*Ber.* 46, 1732). Wallach has suggested (*Ann.* 239, 49) a hydrogenated  $C_{10}H_8$  ring for the structure of the polycyclic sesquiterpenes. Semmler wishes to limit this structure to the sub-groups (a). R., M. and M. have furnished the first explt. support to this view by the dehydrogenation of cadinene by S to a  $C_{10}H_8$  hydrocarbon,  $C_{14}H_{18}$  (cf. *C. A.* 15, 3476). They have applied the same treatment to calamene, isozingiberene, and their

new alc. from Java citronella, and in each case obtained the same  $C_{15}H_{14}$ , d. 0.979, b.  $291^{\circ}$ ,  $M_p$   $67.78^{\circ}$ , for which they have proposed the name *cadalene* (A). On applying the same treatment to eudesmol and selinene they obtained, with the elimination of a Me group, in the dehydrogenation, another  $C_{15}H_{14}$  hydrocarbon d. 0.973, b.  $280^{\circ}$ ,  $M_p$   $63.31^{\circ}$ , and called it *eudalene* (B). It was found that all the sesquiterpenes from a single plant source gave either all A or B, but never mixtures. Both A and B are satd. towards Br and cold  $KMnO_4$ . The constitution of A has been fixed by synthesis (cf. following abstr.) as *1,6-dimethyl-4-isopropyl-naphthalene*. It was found to be readily oxidized by  $H_2CrO_4$ , yielding *1,6-dimethyl-1-isopropyl-naphthoquinone*, whose oxime m.  $178^{\circ}$ , and *6-methyl-4-isopropyl-1-naphthoic acid*, m.  $161-2^{\circ}$ , besides some unidentified products. Semmler (*Ber.* 47, 2555) has shown from work on *copaene* (tricyclic), which gives cadinene dihydrochloride with HCl, that the double bond in cadinene must be in the following



position: R. *et al.*, have found that the monocyclic terpene zingi-

berene (C) gave with S the  $C_{15}H_{14}$  hydrocarbon A. Semmler (*Ber.* 46, 1814) had already shown that C gave with acids the bicyclic isozingiberene. Thus the formation of A on treatment with S is not sure proof of the existence of the  $C_{15}H_{14}$  configuration in the original hydrocarbon. But since A can be obtained from mono-, di-, and tricyclic sesquiterpenes it must be regarded as bearing the same relation to them that *p*-cymene coes to the normal terpenes. The basic principle of all the structures is the coordination of isoprene residues, rubber being the highest polyterpene. IV. **Synthesis of cadalene.** L. RUZICKA and C. F. SEIDEL. *Ibid* 369-75.—This synthesis was carried out to fix definitely the structure of *cadalene* (A) the  $C_{15}H_{14}$  hydrocarbon obtained by the dehydrogenation of various sesquiterpenes with S. Starting with carvone,  $BrCH_2CO_2Et$ , and Zn, R. and S. prepd. ethyl 1-methyl-4-isopropylphenyl-2-acetate,  $b_{12}$   $145^{\circ}$ . This was reduced with Na to the alc.,  $b_{12}$   $145-150^{\circ}$ , and the bromide of the latter treated with  $CHNa(CO_2Me)_2$ , the product sapond. and distd., yielding  $\alpha$ -methyl- $\gamma$ -[1-methyl-4-isopropylphenyl-2]-butyric acid,  $b_{11}$   $200-1^{\circ}$ . The acid chloride of the last named compd. gave with  $AlCl_3$  the 1,6-dimethyl-4-isopropyl-5-ketonaphthalene,  $b_{12}$   $160-170^{\circ}$ , which by reduction and subsequent dehydrogenation with S gave *1,6-dimethyl-4-isopropyl-naphthalene*, identical in every way with A, even to the m. p. of the picrate and styphnate. O. B. H.

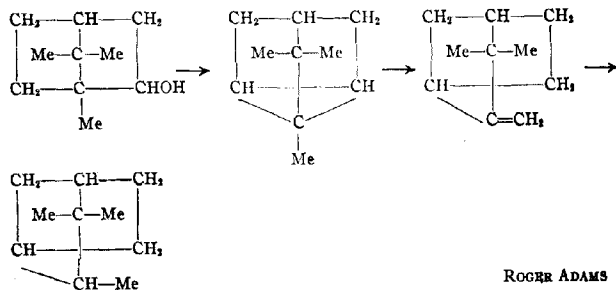
**Interchange of alcohol radicals in esters.** AKIRA SHIMOMURA and J. B. COHEN. *J. Chem. Soc.* 121, 883-7(1922).—A study has been made of the action of menthol or borneol on a variety of esters. Interchange takes place in some cases both with and without Na, in others only when Na is present and in still other no interchange occurs under either condition. With *l*-menthol, no reaction was observed with:  $AcOEt$ ,  $MeCH(CN)CO_2Et$ ,  $PhBrCHCO_2Me$ ,  $PhCH_2CHBrCO_2Me$ ,  $MeEtCHCOCH_2CO_2Et$ ,  $CH_3(CO_2Et)_2$ ,  $(CH_3CO_2Et)_2$ , *o*- $MeC_6H_4CO_2Me$  or *p*- $MeC_6H_4CO_2Me$ . Reaction in the presence of Na was observed with:  $PhCH_2CO_2Me$ (small),  $PhCH_2CO_2Et$ (small),  $PhCICHCO_2Me$ ,  $AcCH_2CO_2Et$ ,  $(CO_2Et)_2$  and *m*- $MeC_6H_4CO_2Me$ (very small). In the absence of Na, reaction occurred with  $AcCH_2CO_2Et$  and  $MeCH_2COCH_2CO_2Et$ . With *l*-borneol, reaction in the absence of Na occurred with  $AcCH_2CO_2Et$ . No reaction occurred with *l*-AmOH and  $MeEtCHCOCH_2CO_2Et$  in the presence of Na. C. J. WESS

**Oxidation of menthone with ferric chloride.** Y. ASAHINA and S. MITTHORI. *J. Pharm. Soc. Japan*, No. 482, 255-63(1922).—By boiling 50 g. menthone and 280 g. hydrated  $FeCl_3$  in 500 cc.  $AcOH$  (50%) for 1.5 hrs. under a reflux condenser, A. and M. obtained cryst. buchu camphor,  $C_{15}H_{16}O_2$  (A), m.  $82$ , sol. in all org. solvents, and insol.

in  $H_2O$ , gives in alc. a dark green color with  $FeCl_3$ , and reduces  $NH_4AgNO_3$ . The A prepd. from buchu leaves showed similar properties. According A. and M., the  $CH_2$  next to the ketonic group is first oxidized to the diketone, which goes over to A by rearrangement. A is known to give two oximes—one m.  $156^\circ$  (Kondodow and Bjalobrzeczski), and the other m.  $125^\circ$  (Semmler and Mackensie). Attempts to produce the oxime either by K.'s or S.'s methods resulted negatively. A similar oxidation of tetrahydrocarvone (carvomenthone) by  $FeCl_3$  did not produce A. By heating 2 g. of A and 1.7 g. of  $PhNCO$  at  $80^\circ$  for 4 hrs., A. and S. obtained a urethan, m.  $113^\circ$ , of the compn.  $PhNHCOO(C_{10}H_{16}O)$ , which differs from that obtained by S. and M. (m.  $141^\circ$ ). S. and M. obtained an unsatd. ketonic acid by oxidation of A with  $KMnO_4$ , but failed to obtain the diketonic acid which was suggested by S. and M. to be the intermediate product. A. and M. dissolved 5 g. of A in 50 cc. acetone, and added 6.3 g. of powdered  $KMnO_4$  while shaking, and obtained besides the unsatd. ketonic acid,  $C_{10}H_{14}O_3$ , white needles, m.  $129^\circ$ , of the compn.  $C_{10}H_{16}O_4$ . They are probably the diketonic acid, the intermediate product suggested by S. and M. S. T.

**Constituents of the saffrons. I. Picrocrocine. E. WINTERSTEIN AND J. TELECZKY. *Helvetica Chim. Acta* 5, 376-81 (1922).**—An  $Et_2O$  ext. of saffron yields *picrocrocine* (A), a glucoside hydrolyzing into sugars (B) and a volatile oil (C). A is obtained in 36 g. yield from 1 kg. of plant material. It crystals from  $Et_2O$  or  $CHCl_3$  in glistening, colorless, monoclinic crystals, m.  $154-5^\circ$ , sol. in  $H_2O$  and  $EtOH$ , difficultly sol. in  $CHCl_3$  and  $Et_2O$  and insol. in petroleum ether and  $C_6H_6$ ,  $[\alpha]_D^{20} -50.3^\circ$ . On hydrolysis with 1%  $H_2SO_4$ , A gave 54% of sugar calcd. as *d*-glucose and 46.2% of C with a pronounced saffron odor, b.  $185-205^\circ$ ,  $b_D^{20} 93^\circ$ , optically inactive, colorless and reacts as a ketone. It was purified through the *semicarbazide*, m.  $162-3^\circ$ , this material being decompd. by the method of Tiemann and Schmidt with  $Ph_2O$  to give the saffron oil. The pure oil has  $d_4^{20} 0.985$ ,  $n_D^{20} 1.5242$ , a dispersion  $n_D - n_C 0.02283$ , and the compn.  $C_{15}H_{11}O$  but a ketone of that character is not recorded. From calcs. on this and other compds., using the formula of Lorenz and Lorenz, the mol. refraction indicates it as belonging to the terpene series and closely related to carvone. It also forms a *semicarbazide* and  $H_2SO_4$ -addition compd. very similar to that of terpene. The sugar soln. (B) remaining after the hydrolysis of A was shown to be a mixt. of *glucose* and *fructose* in the ratio of 4 to 1. The investigation is being continued on the saffron dye-stuffs, the *crocins*, which give on hydrolysis *glucose* and *crocetin*. Previous investigators have probably dealt with a mixt. of crocin and A. The physiol. action of A will also be dealt with. J. A. G.

**Catalytic reduction of *d*-camphor. I. S. KOMATSU AND B. MASUMOTO. *Mem. Coll. Sci., Kyoto Imp. Univ.* 5, 225-32 (1922).**—*d*-Camphor, *d*-borneol and *l*-borneol were reduced with H and Ni at  $175-85^\circ$ . In all 3 cases, the chief reaction product was the same, *viz.*, *l*-isocamphane. The following possible mechanism is suggested:



ROGER ADAMS



**Constitution of the carbonium dyes.** H. E. FIERZ. *Ber.* 55B, 429(1922).—In connection with Hantzsch's formulation of carbonium dyes as  $[R_3C]X$  (C. A. 16, 1414), F. points out that he and Köchlin had in 1918 (C. A. 13, 3174) proposed formulating them as complex salts in Werner's sense and that H. had rejected such a formulation as completely impossible (C. A. 13, 2524). C. A. R.

**Molecular transpositions in the alkylhydrobenzoin series and the  $\alpha$ -glycol analogs.** JEANNE LÉVY. *Bull. soc. chim.* 29, 865-78(1921).—To illustrate these transpositions L. studied the effect of 50%  $H_2C_2O_4$ , 66° B $\phi$ . and 49° B $\phi$ .  $H_2SO_4$  and  $P_2O_5$  on methyl- and ethylhydrobenzoin. The  $H_2SO_4$  and  $P_2O_5$  gave, resp., the diethylene oxides of methyl- and ethylhydrobenzoin. L. discusses in detail the reactions. R. CHESTER ROBERTS

**The dehydration of benzylhydrobenzoin.** A. OREKHOFF AND M. TIFFEYNEAU. *Bull. soc. chim.* 31, 253-55(1922).—Benzylhydrobenzoin (A) when dehydrated with  $P_2O_5$  undergoes a semipinacolic transposition and forms triphenylacetone. When A is dehydrated with  $AcCl$ , a ring structure is produced, giving 1,2-diphenylindene.

R. CHESTER ROBERTS

**Singular formation of ketodinitrones and their behavior (preliminary note).** L. ALESSANDRI. *Gazz. chim. ital.* 52, I, 193-9(1922).—The various known ways of obtaining compds. having 2 nitron groups,  $C:N(:O)$ , are reviewed. In extending expts. on the action of  $PhNO$  on compds. with multiple bonds (C. A. 16, 558). A. found that 2 mols.  $PhNO$  acting on 1 mol.  $PhC:CPh$  gave a bright yellow cryst. addition product (A),  $[CPh:N(:O)Ph]_2$ . This addition takes place very slowly at room temp. and if the mixt. is heated side reactions (oxidations) occur. Better results are obtained when the compds. are dissolved in  $C_6H_6$ ,  $AcOH$ , or  $EtOH$ . The reaction is faster in  $CHCl_3$  but the yield is not so good. A boiled with dil.  $H_2SO_4$  gives  $B_2$  and  $p-H_2NC_6H_4OH$  (formed by the transposition of  $PhNHOH$ ). Reduced with  $Hg-Al$  A gives  $(CPh:NPh)_2$ . These expts. establish its constitution.  $NH_4OH$  acting on A (cf. Angeli, *Atti accad. Lincei* 19, I, 650; Alessandri, *Ibid* 19, II, 127) gave a product resembling A although its analysis corresponds to a partial reduction product,  $CPh(:NPh).CPh:N(:O)Ph$  or an addition product of  $(CPh:NPh)_2$  with A. In the formation of A  $PhNO$  reacts like an unsatd. compd. A was also synthesized by another method (cf. Angeli, *et al.*, *Atti accad. Lincei* 20, I, 546) with  $BrMgPh$  thus:  $(CH:N(:O)Ph)_2$  with 2  $BrMgPh$  gives  $[CPhH.N(OH)Ph]_2$  which with O gives A. A. does not consider this reaction mechanism as necessarily correct and discusses other ways of viewing it. Some tests on the action of  $PhNO$  on  $PhC:CCO_2H$  indicate that if they react they do so very slowly. With  $C_6H_5$  and its H substitution products A. believes that  $PhNO$  reacts otherwise. In fact with  $C_6H_5$  in  $Me_2CO$ ,  $PhNO$  reacts very slowly and if  $KOEt$  is added as a catalyst oxanilide, the isomer of the aldodinitrone of  $[CH:N(:O)Ph]_2$ , was obtained. This reaction is difficult to explain. The absence of the H of the aldodinitrones in ketodinitrones presumably accounts for some of the differences in their transformation products. The work is to be extended in several directions.

E. J. WITZEMANN

**The structure of organic compounds.** W. H. BRAGG. *Proc. Phys. Soc. London* 34, I, 33-50(1921).—X-ray spectrometric data upon individual crystals and upon powders are recorded for  $C_{10}H_8$  and anthracene and various derivs., such as  $\alpha$ - and  $\beta$ -naphthol and acenaphthene. On the hypothesis that the  $C_{10}H_8$  and  $C_{10}H_8$  rings are actual structures having definite size and form which are built as a whole into the org. substance in which they occur, unit cells are given for these crystals. RALPH W. G. WYCKOFF

**Elimination of aromatically combined hydrogen with the union of aromatic nuclei by means of aluminium chloride.** V. Experiments with benzil, stilbene and phenanthrene. R. SCHOLL AND G. SCHWARZER. *Ber.* 55B, 324-30(1922); cf. C. A. 16, 2412.—Phenanthrenequinone (A) can be obtained in 25% yield from  $B_2$  by means of  $AlCl_3$ ; if, which will undoubtedly prove to be the case, the reaction can be applied to

derivs. of  $Bz_2$  also, the new process will afford a new phenanthrene synthesis method which can be set besides Pschorr's. The following are the best conditions: an intimate mixt. of 2 g.  $Bz_2$  and 2 g.  $AlCl_3$  is heated 1 hr. at  $120^\circ$  in a tube protected with a  $CaCl_2$  tube, decompd. with cold dil.  $HCl$ , the residue extd. with boiling  $AcOH$ , filtered, the filtrate poured into cold  $H_2O$ , the dried ppt. freed from tarry impurities with cold  $Et_2O$ , again dried, digested with com.  $NaHSO_3$  soln. +  $1/8$  vol. alc. and the A pptd. with  $HCl$  or  $Na_2CO_3$ . Besides A there are formed, especially if the  $Bz_2$  is heated several hrs. at  $80-100^\circ$  with 2-5 parts  $AlCl_3$ , 2 products sol. in  $NaOH$  with yellow-red to brown color, one of which is pptd. by atm.  $O$ ,  $K_3Fe(CN)_6$  or  $NaOCl$ , the other by acids. Desoxybenzoin heated with  $AlCl_3$  at  $100^\circ$  remains practically completely, at  $200^\circ$  to a large extent, unchanged.  $PhCH:CHPh$ , as already indicated by Liebermann and Mitter (C. A. 6, 2602), is converted by  $AlCl_3$ , even at the temp. of boiling  $CS_2$ , into a trimer, amorphous yellow flocks from  $C_6H_6$ -petr. ether, apparently slowly autoxidizes at  $100^\circ$ , mol. wt. in boiling  $C_6H_6$  579 (P. and M., who give 1498 in freezing  $C_6H_6$ , used a 1.5% soln., which is far above the soly. limit in even boiling  $C_6H_6$ , so they probably had a colloidal soln.), sinters about  $165^\circ$ , carbonizes at higher temps., forms yellowish solns. with very faint dirty green fluorescence (possibly due to impurities), difficultly sol. in concd.  $H_2SO_4$  with yellow-brown color, forms no picrate, reduces aq.  $KMnO_4$  slowly,  $CrO_3$  in  $AcOH$  rapidly, on boiling without yielding definite degradation products; heated 24 hrs. at  $150^\circ$  with 50 parts  $HNO_3$  (d. 1.15) it gives a yellow amorphous acid, apparently  $(C_6H_5O_2)_x$  (possibly benzildicarboxylic acid or a mixt. of different benzildicarboxylic acids), sol. in soda with yellow color which becomes red-yellow, with loss of  $CO_2$ , on heating. From  $AlCl_3$  under  $CS_2$  boiled 8 hrs. with 2 parts phenanthrene is obtained a yellow amorphous substance  $(C_{10}H_8)_x$ , decomp. about  $225^\circ$ , is turned almost black. without dissolving, by  $H_2SO_4$  dissolves on heating with a dirty violet, then a dirty green color, mol. wt. in boiling  $C_6H_6$  662 in 0.63% to 885 in 1.2% soln., converted by  $HNO_3$  (d. 1.41) at  $-8^\circ$  into a  $NO_2$  compd. insol. in the acid. VI. Experiments with phenol ethers and diphenylmethane. ROLAND SCHOLL and CHRISTIAN SEER. *Ibid* 330-41.—As was expected the phenol and especially the naphthol ethers lend themselves much better than the parent hydrocarbons to condensations of the aromatic nuclei by elimination of aromatically bound H by means of  $AlCl_3$ , the reaction occurring at room temp. in  $PhNO_2$ . The  $PhNO_2$  plays a material role in these reactions;  $AlCl_3$  alone does not attack the phenol ethers at room temp. and at higher temps. (a little above  $100^\circ$ ) it first dealkylates the ethers (at least the simple phenol ethers). In the presence of  $PhNO_2$  the condensation of the nuclei proceeds with such a velocity that the ether- and ester-cleaving action of the  $AlCl_3$  cannot manifest itself. The  $PhNO_2$  probably forms with the ethers mol. compds.  $RNO_2 \dots PhOMe$ , a reaction facilitated by the  $AlCl_3$  which thus plays a double part (also probably by forming easily dissociated mol. compds.). From 10 g.  $\alpha$ - $C_{10}H_7$ - $OMe$  in cold dry  $PhNO_2$  with 10 g.  $AlCl_3$  is obtained after 16 hrs. 7 g. 4,4'-diethoxy-1,1'-binaphthyl, leaflets from  $C_2H_5$ - $EtOH$  (2:1), m.  $212-3^\circ$ , also obtained exclusively in the presence of  $ClCO_2Et$  which, owing to the ester-cleaving action of  $AlCl_3$ , behaves as an alkyl chloride in the Friedel-Crafts synthesis. 4,4'-Dimethoxy-1,1'-binaphthyl (1.6 g. from 5 g.  $\alpha$ - $C_{10}H_7$ - $OMe$ ), needles, m.  $252-3^\circ$ . The 2,2'-( $MeO$ ) $_2$  isomer, m.  $190-1^\circ$ , is obtained in only 0.1 g. yield from 2 g.  $\beta$ - $C_{10}H_7$ - $OMe$ .  $m$ - $C_6H_4$ ( $OMe$ ) $_2$  (20 g.) with 20 g.  $AlCl_3$  in  $PhNO_2$  gives after 8 hrs. 0.5 g. of diresorcinol tetramethyl ether, long brown needles from dil.  $MeOH$ , m.  $124^\circ$ . Anthracene and phenanthrene also react with extraordinary ease with  $AlCl_3$  in  $PhNO_2$  but no definite products could be isolated. In the case of  $CH_2Ph_2$  (without a solvent and at room temp.), aromatically bound H is also eliminated, not alone, however, but in combination with Ph, the products being  $C_6H_5$  and anthracene; probably *o*- and *p*- $C_6H_4$ ( $CH_2Ph$ ) $_2$  and *meso*-dihydroanthracene (A) are intermediate products; from the yield of  $C_6H_5$  (1 mol. per mol.  $Ph_2CH_2$ ), the *p*- $C_6H_4$ ( $CH_2Ph$ ), probably also reacts further with elimination of  $C_6H_5$ . That A is an

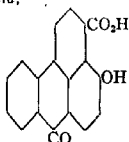
intermediate product is indicated by the fact that A and  $\text{AlCl}_3$  with or without  $\text{C}_6\text{H}_6$  as solvent yield after 0.5 hr. at room temp. 72% anthracene.

C. A. R.

**Electrochemical study of the reversible reduction of organic compounds.** J. B. CONANT, H. M. KAHN, L. F. FISGER AND S. S. KURTZ, JR. *J. Am. Chem. Soc.* **44**, 1382-96(1922).—The reduction of the salts of the  $\alpha$ - and  $\beta$ -mono- and 1,5-, 1,8-, 2,6- and 2,7-disulfonic acid derivs. of anthraquinone, which are  $\text{H}_2\text{O}$ -sol. and related to the vat dyes, by  $\text{TiCl}_3$  and by  $\text{Na}_2\text{S}_2\text{O}_4$  is reversible not only in acid but also in alk. solns. and their oxidation-reduction potentials were readily detd. over a wide range of H-ion concn. The results are in general accord with the equation (1)  $\pi = \pi'_0 + 0.0295 \log \{[A]/[AH_2]\pi - 0.0295 \log K_1K_2 + 0.059 \log [H^+] + 0.0295 \log \{K_1(K_2 + [H^+]/[H^+]^2) + 1\}$  where A is the oxidized,  $AH_2$  the reduced form and  $[AH_2]_T$  the total concn. of reduced material. To test the applicability of the equation, the e. m. f. of the 2 following types of cells was measured:  $0.1 N \text{ HgCl} | \text{KCl} | [H^+] A + AH_2 \text{ Pt}$  and  $0.1 N \text{ HgCl} | \text{KCl} | [H^+] H, \text{ Pt}$ . The mixt. of oxidized and reduced material was obtained by adding definite increments of the reducing agent to a soln. of the oxidized form; the H-ion concn. was controlled by means of buffer solns. The validity of the exptl. method was shown by prep. *sodium diacetylanthraquinol- $\beta$ -sulfonate*, which is stable in the air, hydrolyzing it to the anthraquinol and measuring the potential of mixts. of this with the anthraquinone. Since the reduced compds. are very weak acids (of course, it is the dissociation of the weak phenolic groups of the reduced compd. which are dealt with; the  $\text{SO}_3\text{H}$  groups are so strongly acidic that they can be neglected in the discussion), in acid solns. the last member of equation (1) becomes negligible and  $[AH_2] = [AH_2]_T$ , and since  $\pi = \pi'_0 + 0.059 \log [H^+] + 0.0295 \log [A]/[AH_2]$ ,  $\pi'_0 = \pi'_0 - 0.0295 \log K_1K_2$ ;  $K_1K_2$  can be calcd. directly from this last equation and values for  $K_1$  obtained by solving equation (1) for each point on the graph (oxidation-reduction potential plotted against H-ion concn.) where it bends in alk. soln.

C. A. R.

**Derivatives of 2-hydroxybenzanthrone.** I. C. G. BRADSHAW AND A. G. PERKIN. *J. Chem. Soc.* **121**, 911-22(1922).—When 2-hydroxyanthraquinone is heated under pressure with NaOH and dextrose, erythritol,  $\text{C}_6\text{H}_5(\text{OH})_3$ , mannitol or levulose, 2-hydroxybenzanthronecarboxylic acid,

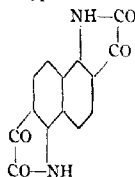


is formed, fine needles, sinters about  $275^\circ$ , fuses  $315^\circ$ . Crystn. from  $\text{Ac}_2\text{O}$  gives the lactone (A), orange-yellow needles, m.  $315-7^\circ$ . *Diethylamine salt*, from A and  $\text{Et}_3\text{NH}$ , large, orange-yellow leaflets. *Anilide*, fine, flat, yellow needles, m.  $274-6^\circ$ , the alk. soln. of which has a green fluorescence. *Acetate*, pale yellow, gradually decomps. on heating. *Dimethyl derivative*, long yellow needles, m.  $185-6^\circ$ .  $\text{FeCl}_3$  in  $\text{AcOH}$  gives the *ferric chloride oxonium salt*, scarlet mass of fine needles. *Stannic chloride salt*, hair-like, scarlet needles. *Chloroplatinate*, bright red prismatic needles. 10% KOH splits off both Me groups. A practically pure *methoxycarboxylic acid* was obtained by the action of 10 parts cold  $\text{H}_2\text{SO}_4$  for 3 hrs., m.  $277-9^\circ$ . Distn. with Zn dust gave benzanthrone. The oxidation of the di-Me ether with  $\text{CrO}_3$  gives *methyl 2-methoxyanthraquinone-1-glyoxylate*, plates, m.  $267-8^\circ$ , which upon sapon. with alc. KOH gave 2-methoxyanthraquinone-1-carboxylic acid (C. A. **14**, 3221). Other products of the reaction are: 2,2'-dihydroxydianthraquinone (?),  $\text{C}_{28}\text{H}_{18}\text{O}_4$ , orange-red needles, which decomp. above  $300^\circ$ , sol. in  $\text{H}_2\text{SO}_4$  with bluish violet color and in dil. alkalies with red tint. *Diacetate*, orange leaflets, partly fuses between  $160-70^\circ$ , then solidifies and m.  $278^\circ$ . *Dimethyl ether*, needles, m.

276°, which readily form oxonium salts with ferric and stannic chlorides, minute, brown needles. Another product is the compound  $C_{21}H_{14}O_4$ , the acetate of which forms fine yellow needles, decomp. about 300°, and a compound  $C_{21}H_{14}O_4$ , the acetate of which forms needles, m. 302–3°. The same results are obtained by starting with 3-hydroxyanthranol. It is difficult to understand the action with  $C_2H_5(OH)_2$ , containing, as it does, only 3 of the 4 necessary C atoms.

C. J. WEST

**A naphthalene diisatin.** JH. MARTINET AND F. VACHER. *Bull. soc. chim.* 31, 435–40 (1922).—Isatin derivs. of the type



may be prepd. by condensation of 1,5- $C_{10}H_7(NH_2)_2$  with Et mesoxalate followed by sapon. and loss of  $CO_2$ . 1,5-Naphthobis- $\beta,\beta'$ -dicarboethoxydioxindole (A) was prepd. by boiling for 0.5 hr. 1 part  $(HO)_2C(CO_2Et)_2$  in 3 parts glacial AcOH with 0.5 part of  $C_{10}H_7(NH_2)_2$ . Crystals sepd. on addition of  $H_2O$ , insol. in PhH,  $Et_2O$ , AcOH,  $C_2H_5Cl$ ,  $Me_2CO$ , darken 220° and char 300°, give an intense violet color with  $H_2SO_4$ . Diacetyl derivative (B), prepd. by boiling A with 10 parts of  $Ac_2O$  in the presence of cryst. NaOAc, white crystals, does not m. below 300°. Tetraacetyl derivative, prepd. like B but using fused instead of cryst. NaOAc, white crystals, infusible below 300°. 1,5-Naphthobis-dioxindole (C), prepd. by warming A with dil. NaOH in H, then acidifying with HCl and decolorizing with C, crystals, difficultly sol. in EtOH and the usual solvents, infusible below 300°. 1,5-Naphthodiisatin (D) is prepd. by warming A with NaOH and stirring in air. The soln. becomes green, then violet and finally yellow. A violet ppt. forms on diln. and neutralizing with HCl, insol. in  $H_2O$ , EtOH, sol. with reddish violet color in AcOH and in pyridine, violet in  $H_2SO_4$ . A drop of thiophene or carbazole added to the  $H_2SO_4$  soln. gives an intense blue color. Monophenylhydrazone, prepd. by boiling D with AcOH and  $PhNHNH_2$ , insol. carmine-red powder, infusible below 360°. Diphenylhydrazone, prepd. by boiling D with excess of  $PhNHNH_2$ , yellowish red insol. powder, infusible below 360°. In alk. soln. with exclusion of air an equimol. mixt. of C and D forms a difficultly sol. green product contg. Na. This may help explain the nature of the products formed in the well known oxidation in the air of the dioxindoles in alk. medium.

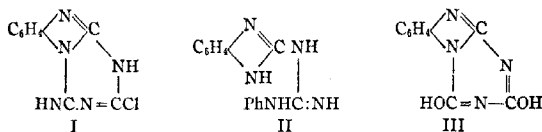
A. W. DOX

**Some ketones of the pyrazole series.** C. A. ROJAHN. *Ber.* 55B, 291–4 (1922).—In an earlier work (C. A. 11, 3261), it was found that in the application of the Friedel-Crafts ketone synthesis to 1-phenyl-3-methyl-5-chloropyrazole the yield of 4-acyl deriv. varied from 1 to 90% depending upon the nature of the acid chloride used. With aliphatic acid chlorides and aromatic sulfonyl chlorides there was no reaction at all, likewise with chloropyrazoles not substituted in position 1. A further study of the influence of the other substituents of the pyrazole nucleus on the reactivity of the 4-H atom towards  $BzCl$  in the ketone synthesis has now shown that only those chloropyrazoles having an aromatic substituent in position 1 react, 1-tolyl-3-methyl-5-chloropyrazole (A) giving 90% of the ketone. Whether the 3-substituent is aliphatic or aromatic seems to make no great difference, 1,3-diphenyl-5-chloropyrazole (B) giving the ketone almost quant. The 5-pyrazolones do not form the ketones at all, 1-phenyl-3-methyl-5-pyrazolone (C) giving the 5-O-Bz deriv. and 3-methyl-5-pyrazolone (D) the 1-N-5-O-di-Bz deriv., both of which are easily hydrolyzed by boiling alkali and can also be obtained

by the Schotten-Baumann method; they easily form 4-Br derivs. The above 4-ketones, heated in a tube with  $N_2H_4 \cdot H_2O$ , condense to bipyrazoles. *1-p-Tolyl-3-methyl-4-benzoyl-5-chloropyrazole* (E), from 17 g. A, 20 g.  $BzCl$ , 75 cc.  $CS_2$  and 25 g.  $AlCl_3$  heated 6 hrs. at 60–5°, 8-sided plate-shaped crystals from dil. alc., m. 70°. *1,3-Diphenyl-4-benzoyl-5-chloropyrazole*, from B (which m. 56°, not 49° as given in the literature), needles from dil. alc., m. 127°,  $b_{25}$  340–5°. *1-Benzoyl-3-methyl-5-benzoyloxy-pyrazole*, long needles from dil. AcOH, m. 128°, completely hydrolyzed to D by 10% NaOH after 3 hrs. on the  $H_2O$  bath, gives with the calcd. amt. of Br in AcOH the 4-bromo derivative, long needles, m. 167°. *1-p-Tolyl-3-methyl-4-phenylbipyrazole*, from E heated 12 hrs. in a sealed tube at 160–75° with 50%  $N_2H_4 \cdot H_2O$ , felted needles from AcOH, m. 244°, yield, quant. *1,3,4-Triphenylbipyrazole*, felted needles from AcOH, m. 233°. C. A. R.

**The hydrolysis of antipyrine salicylate.** I. M. KOLTHOFF. *Rec. trav. chim.* 41, 135–44 (1922).—The fact that salicylic acid (A) forms a compd. with antipyrine (B) is attributed by several authors to the existence of a phenol group in this acid; the  $CO_2H$  has no influence. Miss Regenbogen (*Diss. Utrecht 1918*) showed that the  $CO_2H$  group gives rise to this compd. Since A is a moderately strong acid and B is a weak base antipyrine salicylate (C) should behave like a salt strongly dissociated hydrolytically in aq. soln. C was found to be strongly hydrolyzed and the laws of hydrolysis were found to be applicable. The product of the ions is a const. The product of the concns. of the hydrolyzed substances is also a const. (const. of soly. or hydrolysis product). The dissociation const. of B was detd. by detg. the electrical cond. of mixts. of  $HCl + B$  from which the dissociation const. of B was calcd. The same result was obtained more easily by detg. the H ion concn. colorimetrically in the mixts. and in  $HCl$  since even weak bases can combine with H ions thus:  $BOH + H^+ \rightleftharpoons B + H_2O$ . The quant. relation involved is expressed thus:  $[BOH] [H^+] / [B^+] = K_{H_2O} / K_B$ , in which  $K_B$  is the dissociation const. of the base. This const. for B is  $K_B = 4 \times 10^{-13}$ . The value of the same const. as detd. for  $CO(NH_2)_2$  is  $10^{-14}$ . The soly. of C at 18° is  $1.32 \times 10^{-3}$  mol.; the ion product is  $6.2 \times 10^{-6}$ ; the soly. const.  $[BOH] [HA]$  is  $1.2 \times 10^{-4}$ . In solns. of B the soly. of C diminishes in conformity with the theory. Theoretically A should have little influence on the soly. of C; this was confirmed experimentally. E. J. W.

**The action of cyanogen halides on phenylhydrazine.** VI. The chloride of *o*-phenyleneammethyl chloride. G. PELLIZZARI. *Gazz. chim. ital.* 52, I, 199–206 (1922).—In a previous paper (C. A. 15, 3076) P. showed that *o*-phenylene- $\alpha$ , $\beta$ -dicyanoguanidine (A) easily adds  $NH_3$  and primary amines to give derivs. of isoameline (B). He has now found that A reacts with  $HCl$  giving a chlorinated melaminic deriv., *o*-phenyleneammethyl chloride (I). The mechanism



previously given for the formation of A differs somewhat from that involved in the formation of B. P. discusses this briefly and states that additional evidence supporting the interpretation previously given will be published shortly. In formula I it is considered that the Cl atom is bound to the C atom that corresponds to the  $\beta$ -CN group in A; this was detd. by the fact that on hydrolysis it gives II of known constitution, which is also obtained from isomelamine. I boiled with  $HCl$  gives phenylenemelaminic acid (III). Phenyleneammine with  $HNO_2$  also gives III. Hot alkalis acting on I give phenyleneguanitorea (C), which was previously obtained from phenylene- $\beta$ -cyanoguanidine (D) and  $HCl$ . C obtained from D sepd. as shining needles from EtOH but as anhyd. scales from

$H_2O$ . C obtained in alk. soln. is pptd. with AcOH or  $CO_2$  and crystd. from  $H_2O$  as long anhydrous needles, but when left in the  $H_2O$  they take up 2  $H_2O$  of crystn. The scales derived from D remain unchanged in  $H_2O$ . Otherwise C from the 2 sources behaves the same in a no. of tests that are given. 10 g. crude A were purified by suspending in  $H_2O$  with  $NH_4OH$ , filtering and pptg. with HCl. The fine powder (without drying) was transferred to a glass-stoppered bottle and agitated with 40 cc. fuming HCl. After 24 hrs. the mixt. was heated to  $80^\circ$ , unchanged A was filtered off, the filtrate was neutralized with  $Na_2CO_3$  and the pptd. I filtered off and washed. From EtOH I sepd. as micro-crystals, yellows at  $220^\circ$  but does not m. When dried in air D contains 0.5 mol.  $H_2O$ . 2.5 g. I boiled in 60 cc.  $H_2O$  + 2 cc. HCl seps. 1.6 g. III in a few mins. as small needles that do not m. but decomp. on Pt foil at  $300^\circ$ . 1 g. phenyleneammeline hydrochloride warmed in 300 cc.  $H_2O$  + 6 cc. HCl gave a soln. through which  $N_2O_5$  was passed. After 48 hrs. the fine crystals of III were filtered off. III appears to exist in 2 desmotic forms.

E. J. WITZEMANN

**Benzobisthiazoles.** S. R. H. EDGE. *J. Chem. Soc.* **121**, 772-5 (1922).—The interaction of  $m\text{-}C_6H_4NHAc$  and  $P_2S_5$  in dry  $C_2H_6$  gives a mixt. of the *mono-* and *dithioacetyl-m-phenylenediamines* (A), minute, needle-shaped crystals, m.  $181.5^\circ$ , in which the ratio is 7 mols. dithio- to 2 mols. monothio- compd. The mixt. can only with difficulty be resolved into its components. Four crystns. from EtOH gave the *dithio derivative*, slender, yellow crystals, m.  $194^\circ$ . A in dil. NaOH, oxidized with  $K_2Fe(CN)_6$ , gave *2,6-dimethylbenzobisthiazole* (maybe *2,7-dimethylbenzobisthiazole*), pale yellow, b.  $240^\circ$ , b.  $342-4^\circ$ , m.  $106^\circ$ . It is a monobasic acid, forming a *hydrochloride*, stout crystals, m.  $215^\circ$ , and a *methiodide*, m.  $236^\circ$  (decompn.). *2,6-Dimethyl- $\beta$ -benzobisthiazole dimethiodide*, on the other hand, is readily formed from the components, yellow powder, m.  $238^\circ$  (decompn.).

C. J. WEST

**Ring closure in sulfur-containing dicarboxhydrazides. II. Thiourazole.** F. ARNDT, E. MILDE and F. TSCHENSCHER. *Ber.* **55B**, 341-56 (1922); cf. *C. A.* **16**, 1094.—It was established as a general rule in the earlier paper on the ring closure in S-containing dicarboxhydrazides that when cleavage occurs at one side of the mol. and the 5-membered ring is formed through one of the atoms on the C atom on the other side of the mol. it is the S which enters the ring (with formation of thiobiazoles) in neutral and acid medium and the N (forming triazoles) in alk. medium. The validity of the rule could not at the time be detd. for those cases in which the primary cleavage, considered by itself alone, left not a cyanamide but a mustard oil or isocyanate group, as in the compds. studied at that time no such cleavage occurred in alk. soln. In the meantime, however, a no. of such cases have become available and the rule has been confirmed for these also; the same cleavage which on heating alone or with acids leads to thiobiazoles gives in alk. medium the isomeric triazoles (dithio- or monothiourazoles or their substitution products in these new cases); only in one instance was a thiobiazole obtained along with the triazole.  $PhNHCONHNHCSNH_2$ , m.  $217-8^\circ$ , boiled 30 min. under a reflux with 1.33 times the amt. of 2 N NaOH necessary for soln. gives  $PhNH_2$ ,  $NH_3$ , and, on acidifying with concd. HCl,  $H_2S$ . The cleavage of the  $NH_2$  leads to the formation of *4-phenylthiourazole* (A), which seps. on cooling and scratching; its behavior (strong acid, methylation, disulfide formation) agree with the view that it is A. The cleavage of  $PhNH_2$  (which is the main reaction) is accompanied by the formation of *thiourazole* (B),  $NH_2CO.NH.NH.CS$ , which is isolated as the *monosodium salt*, prisms with 3  $H_2O$ ,

by concg. the filtrate from A until NaCl begins to sep., making alk. with concd.  $NH_4OH$ , filtering hot, cooling and scratching; free B, obtained by scratching a satd. soln. of the Na salt in cold 4 N HCl, crystals from dil. HCl or from alc. containing a few drops of concd. HCl, m.  $206^\circ$  (foaming), is strongly acid; *trisilver salt*, from the Na salt and an excess of  $NH_3 \cdot AgNO_3$ , deep yellow ppt. Treated in alc. with alc. I until the I color

is no longer discharged or in aq. acid soln. with  $\text{FeCl}_3$ , **B** forms *thiourazole disulfide*,  $[\text{NH.CO.NH.N:CS-}]_n$ , needles with 2  $\text{H}_2\text{O}$  from dil. acids, m.  $246^\circ$  (decompn.), easily

sol. in  $\text{NH}_4\text{OH}$ , also in concd.  $\text{HCl}$ , being reprecipitated on diln. (owing to hydrolysis), gives in  $\text{NH}_4\text{OH}$  with  $\text{K}_3\text{Fe}(\text{CN})_6$  an orange color and evolves  $\text{N}$ ; in  $\text{NaOH}$  the color hardly appears and the  $\text{N}$  evolution is more pronounced; this behavior is apparently shown by all triazoles which of themselves, according to their structure, are capable of an "urazole reaction" but contain also a  $\text{C:O}$  adjacent to the hydrazo group (e. g., urazole); the reaction is designated the "urazole reaction." *Methyl ether of B*,  $\text{NH.CO.NH.N:CSMe}$ ,

from the Na salt in  $\text{H}_2\text{O}$  with  $\text{Me}_2\text{SO}_4$ , platelets, m.  $192-3^\circ$ , easily sol. in  $\text{NH}_4\text{OH}$ , sol. in concd.  $\text{HCl}$  (hydrolyzing with  $\text{H}_2\text{O}$ ), gives the "urazole reaction" with  $\text{K}_3\text{Fe}(\text{CN})_6$ . The compd. m.  $177^\circ$ , described in the textbooks as **B**, obtained by Freund (*Ber.* 29, 2509) from  $\text{H}_2\text{NCONHNHCSNH}_2$  with concd.  $\text{HCl}$  (and also in small amt. from  $\text{PhNHCONHNHCSNH}_2$  with  $\text{HCl}$ ) is therefore not identical but isomeric with **B** and is consequently *iminothiobiazolone*,  $\text{CO.NH.NH.C(:NH).S}$ . **B** is obtained more con-

veniently and in better yield by boiling with a slight excess of 2  $N$   $\text{NaOH}$  (whereby  $\text{MeSH}$  is evolved) the *hydrazide*  $\text{MeSCONHNHCSNH}_2$ , cryst. powder, m.  $208^\circ$  (decompn.), easily sol. in  $\text{NaOH}$ , difficultly in  $\text{NH}_4\text{OH}$ , which is precipitated by shaking 2 mols.  $\text{H}_2\text{NCSNHNH}_2$  in just the necessary amt. of hot  $\text{H}_2\text{O}$  with 1 mol.  $\text{ClCOSMe}$ . The *4-phenyl-iminourazole (C)*,  $\text{PhN.CO.NH.NH.C(:NH).S}$ , whose formation should accompany the

cleavage of  $\text{H}_2\text{S}$  noted in the action of the boiling  $\text{NaOH}$  on the hydrazide  $\text{PhNHC-ONHNHCSNH}_2$  was not isolated from the reaction mixt. but is obtained smoothly and exclusively (along with  $\text{MeSH}$ ) by boiling with  $\text{NaOH}$  the *S-methyl ether* of the hydrazide,  $\text{PhNHCONHNHC(:NH)SMe}$ , prepd. from the hydrazide in  $\text{NaOH}$  with  $\text{Me}_2\text{SO}_4$ , silky needles from alc., m. about  $147^\circ$  (foaming), easily sol. in dil.  $\text{H}_2\text{SO}_4$ , forms difficultly sol. salts with  $\text{HCl}$  and  $\text{HNO}_3$ , is reprecipitated unchanged by  $\text{NH}_4\text{OH}$  from  $\text{H}_2\text{SO}_4$  after 30 min. boiling. **C** seps. from  $\text{H}_2\text{O}$  in platelets, m.  $231-2^\circ$ , sol. in concd. mineral acids (in  $\text{HNO}_3$  with pptn. of the nitrate), insol. in dil.  $\text{AcOH}$ , sol. in  $\text{NaOH}$  and concd.  $\text{NH}_4\text{OH}$ , gives in  $\text{NaOH}$  with  $\text{K}_3\text{Fe}(\text{CN})_6$  the "urazole reaction." Whereas in the case of  $\text{PhNHCONHNHCSNH}_2$ , the cleavage of  $\text{NH}_3$  is but a side reaction occurring to only a small degree, it becomes the chief reaction in the case of the *hydrazide*  $\text{PhNHCSNHNHCONH}_2$  (**D**), flat needles from alc., m.  $198^\circ$ , easily sol. in  $\text{NaOH}$ , obtained almost quant. from 5.6 g.  $\text{H}_2\text{NCONHNH}_2$ ,  $\text{HCl}$  and 2.7 g. anhyd.  $\text{Na}_2\text{CO}_3$  in the least possible amt. of hot  $\text{H}_2\text{O}$  warmed with  $\text{PhNCS}$  and the requisite amt. of alc.; boiled 0.5 hr. without a reflux in the necessary amt. of 2  $N$   $\text{NaOH}$  it gives almost exclusively **A**, long stout prisms with 1  $\text{H}_2\text{O}$ , m.  $130-6^\circ$  and, anhyd.,  $196^\circ$ , easily sol. in dil.  $\text{NH}_4\text{OH}$ , oxidized in concd. alc. soln. by the calcd. amt. of alc. I to the *disulfide*, needles, m.  $284-5^\circ$ , sol. in  $\text{NaOH}$ , more difficultly in concd.  $\text{NH}_4\text{OH}$ , insol. in acids, does not react in  $\text{NaOH}$  with  $\text{K}_3\text{Fe}(\text{CN})_6$ ; *methyl ether of A*, from **A** in  $\text{NH}_4\text{OH}$  with  $\text{Me}_2\text{SO}_4$ , needles from alc., m.  $207-8^\circ$ , insol. even in concd.  $\text{HCl}$ , sol. in  $\text{NaOH}$  but not in  $\text{NH}_4\text{OH}$ , does not react in  $\text{NaOH}$  with  $\text{K}_3\text{Fe}(\text{CN})_6$ . *S-Methyl ether of D*, could not be obtained cryst., is easily sol. in  $\text{HCl}$ , giving the *Me ether of A* on boiling; boiled a few min. with 2  $N$   $\text{NaOH}$  it gives  $\text{MeSH}$  and *anilinourazole*,  $\text{NH.C(:NPh).NH.NH.CO}$ , m.  $238^\circ$ , insol. in dil. acids,

sol. in concd.  $\text{HCl}$  (in concd.  $\text{HNO}_3$  with brown color and gas evolution), easily sol. in dil.  $\text{NH}_4\text{OH}$ , the soln. giving with  $\text{K}_3\text{Fe}(\text{CN})_6$  a not very intense red color, with no evolution of  $\text{N}$ ; it gives the "urazole reaction" in  $\text{NaOH}$ . *Monophenylhydrazodicarboxythioamide (E)*,  $\text{PhNHCSNHNHCSNH}_2$ , from 6 g.  $\text{H}_2\text{NCSNHNH}_2$  in the least possible amt. of hot  $\text{H}_2\text{O}$  boiled a short time with 7.3 g.  $\text{PhNCS}$  and the requisite amt. of alc., leaflets from alc., m.  $180^\circ$  (yield, almost quant.); boiled 45 min. with 2  $N$   $\text{NaOH}$ , it loses  $\text{NH}_3$

and  $H_2S$ , giving a mixt. of *4*-phenyldithiourazole (**F**) and *4*-phenyliminothiourazole (**G**),  $PhN.C(:NH).NH.NH.CS$ , sepd. by shaking with cold 0.5–1.0 *N*  $Na_2CO_3$  in which **F** is

sol. **F** (the substance described up to 1913 under this name is *anilinothiobisolethiol* (**H**),  $PhN:C.NH.NH.CS.S$ ), seps. from alc. in stout crystals, m.  $216^\circ$  (decompn.) (**H** m.

about  $217^\circ$  but depresses the m. p. of **F** to  $180-5^\circ$ ); *dimethyl ether*, from **F** in  $NH_4OH$  with  $Me_2SO_4$ , long needles from  $C_6H_6$ -ligroin, m.  $132.5^\circ$  (the Me ether of **H** m.  $127^\circ$  and depresses the m. p. of the above di-Me ether to  $90-100^\circ$ ), dissolves easily in dil. acids, forms a difficultly sol. *nitrate*, m.  $141^\circ$ . On oxidation, **F** yields various disulfides; in just the necessary amt. of NaOH with  $K_3Fe(CN)_6$  it gives a yellow ppt. easily sol. with deep yellow color in dil.  $NH_4OH$  (therefore it still contains SH groups), m. around  $160-80^\circ$ , easily sol. in hot AcOH but there seps. from the soln., apparently as the result of further oxidation, a substance much less sol. in AcOH, light yellow crystals, m.  $228^\circ$ , also obtained from **F** and **I** in alc., which is also still sol. in  $NH_4OH$ ; complete oxidation to alkali-insol. products could not be effected. **G** seps. from alc. in long flat needles with 1  $H_2O$ , m. anhyd.  $267-8^\circ$ , easily sol. in NaOH, more difficultly in  $NH_4OH$ , hardly in soda, gives in 2 *N* NaOH with  $Me_2SO_4$  a *methyl ether*, silky needles with 0.5  $H_2O$ , sinters  $117^\circ$ , m.  $165^\circ$  (anhyd.,  $168^\circ$ ), insol. in NaOH, easily sol. in dil. acids (including AcOH), forms a difficultly sol. *nitrate*, m.  $168^\circ$  (decompn.). **G** forms no disulfide in alc. with **I**; in  $NH_4OH$  with  $K_3Fe(CN)_6$  it forms an amorphous ppt., which redissolves, the disulfide being apparently formed and then undergoing decompn.; in NaOH, both **G** and its Me ether give with  $K_3Fe(CN)_6$  a dirty yellow amorphous ppt. C. A. R.

**Opening of the ring in the phenopyrylium series.** HERMAN DECKER AND PAUL BECKER. *Ber.* 55B, 375–94(1922).—The increased interest acquired by the phenopyrylium dyes since it has been shown that they are so widely distributed in plants made a thorough study of non-hydroxylated pyranols seem desirable. The ring opening already observed in some cases was studied more completely, then hydroxyphenopyrylium hydroxides, which also undergo the ring opening, were investigated, and finally some observations on the free dyes were collected which might throw light upon the cause of their colors. The starting material for the first part of the work was the 2,3-diphenylphenopyrylium chloride (**A**) obtained from  $PhCH_2Bz$  and *o*- $HOC_6H_4CHO$ ; the colorless *pyranol* (**B**),  $C_6H_4.CH:CPh.CPh(OH).O$ , obtained from the yellow oxonium hydroxide

gives with cold NaOH the red salt of the chalcone, *cis*- $\alpha$ -phenyl-*o*-coumarinophenone (**C**), *o*- $HOC_6H_4CH:CPhCOPh$ , which on warming in the soln. rearranges into the stable *trans*-isomer ( $\alpha$ -phenyl-*o*-coumarinophenone) (**D**), further action of the NaOH decomp. it into  $HOC_6H_4CHO$  and  $PhCH_2COPh$ . With HCl the above series of transformations can be completely reversed. **B** yields a *methyl alcoholate* (**E**),  $C_6H_4.CH:CPh.CPh(OMe).O$ ,

and **D** gives the *cis*- and *trans*-methyl ethers (**F**), both of which and **E** regenerate **A** with HCl. The ring opening of **B** and the stereoisomerism of **C** and **D** and their ethers is analogous to the behavior of coumarin in alkalis, the resulting acids, coumarinic and *o*-coumaric, being *cis*- and *trans*-isomers, resp. The phenol group makes the hydroxy-chalcones sol. in alkali; they can therefore easily be sepd. from the isomeric pyranols and the course of the ring opening can be followed by the increasing change in color of the soln. In the quinoline series, the quinolanols, the primary isomerization products of the ammonium hydroxides (which have been isolated in many cases), are not so easily sepd. from the *N*-alkyl-*o*-aminocinnamic aldehydes or ketones which are to be expected to result from the opening of the ring. However, in view of the results obtained in the pyranol series, the *trans*-form must be stable and should be capable of isolation if the tendency of the  $NH_2$  to react with the aldehyde group does not lead to dimol. reactions. In any case, by Gerngross' method (action of  $BzCl$  in alk. soln. on quaternary quino-



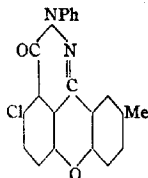
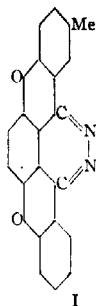
linium salts; *C. A.* 7, 2942) the Bz derivs. of the opened compds. can be isolated. The smooth hydrolysis of pyranols by alkalis affords a means of effecting the stepwise degradation of the natural dyes of unknown structure and detg. whether the Ph group is in the  $\alpha$ - or  $\gamma$ -position. The colorless carbinol bases which have been isolated from the anthocyanidins are probably still closed ring derivs. (anthocyanidanols). **A** (*C. A.* 3, 1004) can be obtained in 88.5% yield (instead of 69%) as the FeCl<sub>3</sub> double salt if, after satg. with HCl, the mixt. is heated 10 min. on the H<sub>2</sub>O bath. To isolate the *o*-coumarophenone, m. 154-6°, the heating is stopped as soon as the max. color is attained and the ketone pptd. with CO<sub>2</sub> or AcOH (yield, practically quant.). **B** (1.8 g. from 3 g. of the FeCl<sub>3</sub> salt of **A** in 25 cc. AcOH slowly dropped into 60-70 parts H<sub>2</sub>O), stout, very faintly yellow tables from AcOH, m. 123-4°, only slightly sol. in 5% HCl or H<sub>2</sub>SO<sub>4</sub>, at once in concd. acids with the yellow color of **A**, quite stable in the air (a sample kept loosely stoppered for 6 yrs. did not change at all); the cryst. **B** is practically insol. in alkalis at room temp. but if rubbed in finely powdered form with 10% NaOH traces dissolve with yellow color; on heating, however, the opening of the ring and formation of the red salt of **D** can easily be detected by the increasing color of the soln. **E**, from **B** boiled a short time with MeOH, m. 75-6°; *ethyl homolog*, similarly obtained with EtOH, m. 77-8°; *propyl compound*, stout prisms from PrOH, m. 70-1°; *isobutyl compound*, reddish prisms, m. 68-9°. On heating with an excess of another alc. they change smoothly into the ether of the 2nd alc.; they can be pptd. from their alc. solns. with 5% NaOH as milky emulsions and boiled 5 min. without an opening of the ring; in hot 18% HCl or cold fuming HCl they form **A**. **B** (1 g.) heated with 25 cc. of 1% NaOH until the max. color is just reached (about 20 min.), dild. with about 10 cc. H<sub>2</sub>O and filtered boiling hot yields the *sodium salt* of **D**, dark red needles with 3 H<sub>2</sub>O, which it loses at about 150°, becoming lighter in color, and m. 194-6°; from the aq. soln. containing a few drops of NaOH CO<sub>2</sub> ppts. the free **D** ( $\alpha$ -salicylaldehydobenzoin, 2-hydroxy-8-phenylchalcone), faintly salmon-red needles from C<sub>6</sub>H<sub>6</sub>-ligroin, m. 154-5° (yield, 80% of the **B**), immediately sol. in cold very dil. NaOH with yellow-red color but in 5-10% NaOH it at once becomes colored with a layer of the insol. red Na salt whereby the least traces in the presence of crystals of **B** can be detected under the microscope. *trans-F* (*trans-2-methoxy-8-phenylchalcone*), from **B** heated 0.5 hr. on the H<sub>2</sub>O bath with 40 parts of 1% NaOH, dild. with an equal vol. of H<sub>2</sub>O, cooled, treated with such an amt. of concd. NaOH that the Na salt just remains in soln., freed from the rest of the **B** by filtration and extn. with Et<sub>2</sub>O and shaken with Me<sub>2</sub>SO<sub>4</sub> added in small portions, faintly yellow needles from 90% alc., m. 141°, gives the yellow color of **A** with concd. HCl only on heating. **D** is partly converted back into **B** by refluxing 0.5 hr. in 20-30 parts PhMe or by heating to its m. p. without a solvent. **C** (*cis-2-hydroxy-8-phenylchalcone*) is obtained by vigorously shaking a fresh emulsion of **B** (*e. g.*, as prepd. by treating **B** in AcOH with 20 vols. H<sub>2</sub>O) with cold dil. NaOH, whereby a large part dissolves with yellow color; very concd. NaOH ppts. an amorphous flocculent yellow salt and CO<sub>2</sub> gives an amorphous ppt. which on ever so cautious crystn. yields **B**, but if the alk. soln. is boiled, CO<sub>2</sub> now ppts. **D**; with Me<sub>2</sub>SO<sub>4</sub> the yellow alk. soln. gives *cis-F*, oil from Et<sub>2</sub>O solidifying to faintly yellow tablets, m. 111-2°, slowly becoming opaque and disintegrating on standing. Attempts to synthesize **D** from 2 g. PhCH<sub>2</sub>COPh, 1.25 g. *o*-HOC<sub>6</sub>H<sub>4</sub>CHO, 8 cc. alc. and 1 g. NaOH by boiling 2.5 hrs. gave a substance sepg. from H<sub>2</sub>O in leaflets, m. 120-1°, which was apparently a *polymerized salicylaldehyde*. 2-Phenylphenopyranol, more or less greenish amorphous powder, sinters 70-80°, obtained like **B**, gives with alkalis *trans*-coumarophenone and, on further warming, HOC<sub>6</sub>H<sub>4</sub>CHO and PhCOMe.

C. A. R.

Absorption spectrum of coloring matters of the flavone group. II. Absorption spectrum of chalcone and its derivatives. YUJI A. SHIBATA AND WILLY NAGAI. *J.*

*Chem. Soc. Japan* 43, 101-22(1922); cf. *C. A.* 13, 440.—S. and Kimotsuki showed in contribution I that the flavone group in 0.0001 *M* soln. shows 2 absorption bands in the ultra-violet zone, and that the waves lengths and characters of the bands are systematically influenced by the no. and positions of its auxochromic group (OH). In this work, the absorption spectra of chalcone, 2', 3'- and 4'-hydroxy-, 2'-hydroxy-4'-methoxy-, 2-, 3- and 4-hydroxy-, 3-methoxy-4-ethoxy-, 4-ethoxy-4'-hydroxy-, and 2'-hydroxy-4,4'-diethoxychalcones and natural naringenin were studied. The conclusions are: In spite of the fact that chalcone and flavone have the same chromophore group, their spectra are quite different, the former having one large band in the ultra-violet region (3300 Å.), and the latter absorbing the light more hypochromatically than the former. The introduction of a OH group in chalcone produces a more complex effect than in flavone. Introduction of a OH group in the Bz nucleus of the chalcone shows almost no effect, while similar introduction in the benzal group produces one or two additional absorption bands. When OH is introduced into both the Bz and benzal groups, one large band is produced, the effect being bathochromic. Spectra of the natural naringenin suggest that it is not a chalcone deriv. S. T.

**Xanthone series.** ANNA MARIE V. DEM KNESEBECK AND FRITZ ULLMANN. *Ber.* 55B, 306-16(1922).—The reaction whereby 2'-hydroxy-3,4,5,6-tetrachloro-2-benzoylbenzoic acid is converted by treatment with alkali into 5,6,7-trichloroxanthone-8-carboxylic acid (*C. A.* 14, 1998) has been applied to the synthesis of dixanthones. From 5 g. 3,6-dichlorophthalic anhydride (A) in 25 cc. (CHCl<sub>3</sub>), and 5 g. *p*-cresol treated in the course of 1.5 hrs. with 15 g. AlCl<sub>3</sub>, the mixt. being gradually heated to 115-20° when about 0.5 of the AlCl<sub>3</sub> has been added and kept 3 hrs. at 120° after it has all been added, is obtained 6.2 g. 2'-hydroxy-5'-methyl-3,6-dichloro-2-benzoylbenzoic acid, light brown needles from xylene, m. 187°, forms faintly brownish solns., orange-yellow in concd. H<sub>2</sub>SO<sub>4</sub>, gives with alkalis sol. yellow salts, is apparently isomeric with the acid m. 173° obtained by Weizmann from A and *p*-MeC<sub>6</sub>H<sub>4</sub>OMe in CS<sub>2</sub> (*C. A.* 4, 2114); 5 g. boiled 2 hrs. under a reflux with 50 cc. of 20% K<sub>2</sub>CO<sub>3</sub> gives 4.1 g. 2-methyl-7-chloroxanthone-8-carboxylic acid (B), faintly yellowish needles from AcOH, m. 286° (decompn.), sol. in concd. H<sub>2</sub>SO<sub>4</sub> with yellow color and green fluorescence; 0.5 g. heated at 280-5° until the evolution of CO<sub>2</sub> ceases yields 0.4 g. of the xanthone, needles from alc., m. 160°, insol. in boiling alkalis, sol. in concd. H<sub>2</sub>SO<sub>4</sub> with yellow color and green fluorescence. 2-Methyl-7-phenoxyxanthone-8-carboxylic acid (0.42 g. from 0.5 g. K<sub>2</sub>CO<sub>3</sub> and 3 g. PhOH boiled until the K<sub>2</sub>CO<sub>3</sub> has dissolved and all the H<sub>2</sub>O driven off, then boiled 0.5 hr. with 0.5 g. B and a trace of "Naturkupper C"), needles from alc., m. 270-80° (gradual decompn.); 0.5 g. boiled under a reflux in 3 cc. C<sub>6</sub>H<sub>6</sub> with 0.38 g. PCl<sub>5</sub>, cooled, treated with 1 g. AlCl<sub>3</sub> and refluxed 15 min. gives 0.4 g. 2-methyldixanthone, yellowish needles from AcOH, m. 349-52°, sol. with yellow color and bright green fluorescence in concd. H<sub>2</sub>SO<sub>4</sub>; 0.2 g. heated 10 min. in 3 cc. C<sub>6</sub>H<sub>5</sub>N with 0.5 g. N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O gives 0.17 g. of the azine (I), long, bright yellow felted needles from alc., m. 273°, forms bright yellow solns., those in alc., C<sub>6</sub>H<sub>5</sub>N and PhCl having a strong green fluorescence, sol. in HCl, deliquescent in AcOH and concd. H<sub>2</sub>SO<sub>4</sub>, the acid solns. being orange-red, is completely pptd. from AcOH by concd. HCl as the hydrochloride, red needles, m. 274° (loss of HCl). 2-Methyl-7-anilinoxanthone (0.43 g. from 0.5 g. B, 3.7 cc. PhNH<sub>2</sub>, 0.5 g. KOAc and a rodlet of CuO boiled 1.5 hrs.), yellow-green needles from AcOH, m. 255-9°, forms yellow-green solns. with blue-green fluorescence. 2-Methyl-7-chloro-*N*-phenylpyridazonexanthone (II) (0.52 g. from 0.5 g. B and 3 cc. PhNHNH<sub>2</sub> boiled 5 min.), yellow needles from AcOH, m. 264-6°, forms yellow solns., deliquesces in H<sub>2</sub>SO<sub>4</sub> with yellow-brown color; 0.5 g. boiled 1 hr. with 5 cc. PhNH<sub>2</sub>, 0.25 g. KOAc and a trace of Cu(OAc)<sub>2</sub> gives 0.5 g. of the 7-anilino derivative, exceedingly slender felted yellow-green needles from AcOH, m. 257-8°, forms yellow-green solns., dark green in H<sub>2</sub>SO<sub>4</sub>. 2'-Hydroxy-5'-methyl-5,6-



*dichloro-2-benzoyl benzoic acid*, from 3,4-dichlorophthalic anhydride and *p*-cresol, crystals from AcOH, m. 265°, sol. in alkalis with yellow, in H<sub>2</sub>SO<sub>4</sub> with brown-red color; 2.5 g. boiled 2.5 hrs. with 20% K<sub>2</sub>CO<sub>3</sub> gives 2 g. *2-methyl-5-chloroxanthone-8-carboxylic acid*, light brown needles from AcOH, m. 289-95°, sol. in H<sub>2</sub>SO<sub>4</sub> with yellow color and green fluorescence, is unchanged by boiling with PhNH<sub>2</sub> and Cu; boiled a short time with 2.5 parts PhNHNH<sub>2</sub> it gives *2-methyl-5-chloro-N-phenylpyridazone-xanthone*, long, slender needles from AcOH, m. 266-71°, forms faintly yellow solns., shows strong, green fluorescence in H<sub>2</sub>SO<sub>4</sub>, is insol. in alkalis and is not changed by boiling with PhNH<sub>2</sub>.

C. A. R.

**3,6-Tetramethyldiaminoselenopyronine.** M. BATTEGAY AND G. HUGEL. *Bull. soc. chim.* **31**, 440-4(1922); cf. C. A. **15**, 1498.—The 3,6-tetramethyldiaminoselenopyronine described in the previous paper should give on oxidation the corresponding selenoxanthone, analogous to xanthone and thioxanthone. On direct oxidation, however, with alk. KMnO<sub>4</sub> only an amorphous yellow mass was obtained which would not crystallize. The selenoxanthone was therefore prepd. through the cyanoselenopyronine. 6 g. of the selenopyronine in 80 cc. H<sub>2</sub>O and 6 g. KCN in 60 cc. H<sub>2</sub>O gave a voluminous brownish violet ppt. which on warming to 65° became darker and granular. This leuco deriv. (yield 4.5 g.) was oxidized in HCl by FeCl<sub>3</sub>. The soln. became blue and gave a ppt. at 80°. Boiling with dil. HNO<sub>3</sub> gave *3,6-tetramethyldiaminocyanoselenopyronine nitrate*, green crystals. Salts of the base exist in both amorphous and cryst. form. There are 3 series of salts, a red salt with fuming H<sub>2</sub>SO<sub>4</sub>, which on diln. gives a green and finally a blue salt. Although very resistant to acids, the color is destroyed by alkalis. The *free base* is best obtained by treatment of the soln. of a salt with KCN in the cold. It is sol. in EtOH, PhH, PhMe and anisole with green dichroism and intense red fluorescence. It exists in 2 forms, a colored form corresponding to an ammonium base and a colorless form with enolic structure. In alk. soln. it oxidizes immediately to *3,6-tetramethyldiaminoselenoxanthone*, greenish yellow crystals, m. 261°; yield 80%.

A. W. Dox

**Pyridinium salts derived from some chloroacetyl amino compounds.** E. DUB. BARNETT AND J. W. COOK. *J. Chem. Soc.* **121**, 792-7(1922).—The prepn. of these compds. was undertaken with a view of studying the tinctorial properties of azo dyes containing this grouping, but it was found that both the ClCH<sub>2</sub>CONH- compds. and the salts from them are so easily hydrolyzed that dyes containing this group would be valueless. The simple ClCH<sub>2</sub>CONH- compds. are best prepd. in the presence of quinoline, since its HCl salt is very easily sol. in H<sub>2</sub>O. The C<sub>6</sub>H<sub>4</sub>N deriv. is readily prepd. by warming the components for 0.5 hr. on the H<sub>2</sub>O bath. *Acetanilide- $\omega$ -pyridinium chloride*, needles from alc.-Et<sub>2</sub>O, m. 245°; *picrate*, lemon-yellow needles from hot H<sub>2</sub>O, m. 134°.

*Aceto-p-toluidide*, pearly leaflets, m. 239–43°; *picrate*, glistening, golden yellow needles, m. 141°. *m-Nitroacetanilide*, decomps. 288–91°; *picrate*, pale yellow needles, m. 199–200°. *p-Nitroacetanilide*, hair-like, pale yellow needles, decomp. 271–2°; *picrate*, pale yellow needles, m. 211°; *nitrate*, sparingly sol. *Aceto-α-naphthalide*, m. 242°; *picrate*, glistening yellow needles, m. 228°. The β-deriv. m. 240–1°, and forms a sparingly sol. *picrate*, m. 174–5°. *p-Chloroacetylaminouazobenzene*, yellow, m. 154°. The *pyridinium chloride* forms small, yellow needles, decomp. 250°. It has no dyeing properties. *4-Chloroacetylaminonaphthalene-1-azobenzene*, orange-red needles, m. 217–8°; the *pyridinium chloride* forms glistening, orange-red needles, decomp. 254°. *p-Chloroacetylaminophenyl chloroacetate*, silky needles, m. 170–1°, insol. in cold dil. NaOH and did not give a pure  $C_8H_7N$  deriv. *Acetyldiphenylamine-ω-pyridinium chloride*, powder, m. 263–7°, giving a *picrate*, small, yellow needles, m. 225–6°, exploding on analysis. *2-Chloroacetylaminonanthraquinone*, yellow powder, m. 189–90°; the *pyridinium chloride* is colloidal and could not be purified. The *nitrate* forms an indistinctly cryst. powder from dil.  $HNO_3$ , decomps. 257–8°; the *picrate*, m. 257–8°, could not be crystd.; the *dichromate* forms an insol. yellow powder which does not m. The action of  $ClCH_2COCl$  upon (*p*- $H_2NC_6H_4$ )<sub>2</sub> led to a yellow product apparently containing 2  $ClCH_2CO$  groups but it could not be purified. *Phenyl acetate-ω-pyridinium chloride*, needles, m. 165–8° (decompn.). *β-Naphthyl acetate derivative*, needles, decomp. 169–70°. *o-Acetoxybenzoic acid derivative*, needles, decomp. 165–8°. C. J. WEST

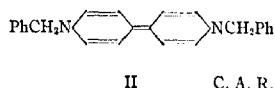
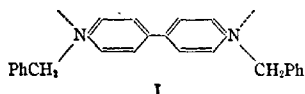
Observations on the work of W. Diltthey and E. V. Meyer concerning 2-methyl-4,6-diphenylpyridine. C. GASTALDI. *Gazz. chim. ital.* 52, I, 169–75(1922).—In connection with the study of the hydrocarbon  $C_{24}H_{22}$  (C. A. 16, 1410) G. has studied the action of  $Ac_2O$  on  $PhCOMe$  in the presence of  $FeCl_3$ , which gives a product concerning the constitution of which G. and Diltthey (C. A. 11, 449) do not agree. G. considers the product to be the  $FeCl_3$  salt of 2-methyl-4,6-diphenylpyrrole (A) while D. considers it to be the corresponding 4-methyl-2,6-diphenyl isomer (B). G. argues that if dypnone reacts with  $BzCl$  in the presence of  $AlCl_3$  as stated by him his formula for A is correct and that  $Ac_2O$  acting similarly on  $MeOC_6H_4COMe$  gives 2-methyl-4,6-*p*-dianisylpyrrole (C). D.'s error depends on accepting an error of E. v. Meyer, who described as 2-methyl-4,6-diphenylpyridine a compd. which is certainly not that. It is well known that pyrrole salts when treated with  $NH_3$  are converted into the corresponding pyridines. D. with A and  $NH_3$  obtained a pyridine different from the 2-methyl-4,6-diphenylpyridine (D) of v. M. and then concluded that A was B. G.'s synthesis of A and C constitutes a new synthesis of pyrrole that takes place in 2 steps: (1) condensation of  $Ac_2O$  with dypnone in the presence of  $FeCl_3$  gives the same compd. that is formed from  $Ac_2O$  and  $MeCOPh$ ; (2) by the action of  $NH_3$  on the pyrrole salt formed D is obtained. The structure of D was detd. by oxidizing it to 4,6-diphenyl-2-pyridinecarboxylic acid (E) and this by the loss of a mol. of  $CO_2$  gives 4,6-diphenylpyridine. 10 g. dypnone + 10 g.  $Ac_2O$  were treated gradually with 8 g.  $FeCl_3$  (sublimed) and after 3 days at room temp. 4–5 g. A,  $C_{24}H_{22}OFeCl_3$ , sepd.; dark green needles from  $Me_2CO$  and  $Et_2O$ , m. 174–5°. A was also obtained from  $MeCOPh + Ac_2O$  and was identical in all reactions but was yellow-brown in color. 18 g. A in 1500 cc.  $H_2O$  was treated with excess  $NH_4OH$  and allowed to stand 12 hrs. The soln. was extd. twice with  $Et_2O$ . The  $Et_2O$  was shaken out 3–4 times with 5%  $HCl$ . The  $Et_2O$  was eliminated with an air current.  $HNO_3$  was then added and the soln. on standing sepd. 9 g. of the nitrate of D, needles, m. 185°. The nitrate decompd. with  $NH_4OH$  gave the free base D, m. 73°. 3 g. D in 200 cc. 5%  $H_2SO_4$  on the  $H_2O$  bath was treated with 9 g.  $KMnO_4$  in the course of 10 hrs. The ppt. was washed with cold satd.  $H_2SO_4$  to remove Mn and then with 5%  $NaOH$ , giving the slightly sol. sodium salt of E. This salt decompd. with  $AcOH$  gave E, needles, m. 150°. A mixt. of 1 part of the Na salt of E + 3 parts of  $CaO$  heated to 400° in an Anschütz

flask *in vacuo* gave **D** as a yellow-red dense liquid. This with 20%  $\text{H}_2\text{SO}_4$  gave the acid sulfate of **D**,  $\text{C}_{17}\text{H}_{12}\text{N}_4\cdot\text{H}_2\text{SO}_4$ , as needles, m.  $245^\circ$  (browning). The study of this base is to be continued.

E. J. WITZEMANN

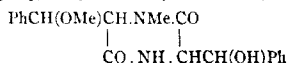
**Free ammonium radicals. III. The existence of *N*-benzylpyridinium.** ERNST WEITZ AND RICHARD LUDWIG. *Ber.* **55B**, 395-413(1922); cf. *C. A.* **16**, 1070.—In paper II it was shown that Hofmann's "*N,N'*-dibenzyltetrahydro- $\gamma,\gamma'$ -dipyridyl" (**A**), obtained by reduction of *N*-benzylpyridinium chloride (**B**) with Na-Hg, changes in  $\text{Et}_2\text{O}\cdot\text{MeOH}$  into a cryst. brown-red substance (**C**) of the same compn., sol. with deep blue color, very sensitive to the air, which was believed to be the free ammonium radical *N*-benzylpyridinium (**D**). The spontaneous bluing of solns. of **A**, their decolorization by atm. O, the reappearance of the blue color, etc. were so reminiscent of the behavior of  $\text{CPh}_3$  that it was at first believed that this was an entirely analogous dissociation of the colorless dimer into the colored pyridinium radical, but important facts not in harmony with this view were pointed out. In the first place, the formation of the "radical" occurs only in the presence of atm. O, and the blue solns. of the crystd. **C** do not regenerate the colorless form. On the other hand, a fact apparently agreeing with the radical structure is that the blue solns. are decolorized by halogens with formation of **B**, identified as the hexanitrocobaltiate. It was then found, however, that the difficultly sol. perchlorates obtained from **B** and from the iodination product of **C**, resp., are not identical, differing in m. p. by about  $160^\circ$ , while the hexanitrocobaltiates previously obtained from the two halides had about the same m. ps. and compns. and depressed each other's m. ps. only very little or not at all. By titration with I of solns. of the crystd. **C**, best in boiling  $\text{Me}_2\text{O}$  or  $\text{CHCl}_3$  in a  $\text{CO}_2$  atm. in an app. which is described, approx. 1 atom I per pyridine nucleus is used up and there is obtained a red, cryst., difficultly sol. iodide (**E**) containing all the I in ionizable form and agreeing approx. in compn. with benzylpyridinium iodide but differing from it in its very much smaller soly. in  $\text{H}_2\text{O}$  and in forming with  $\text{HClO}_4$  the high melting perchlorate. From **E** it is easy again to obtain the dark blue oxidizable soln. by reduction, best in alc. or AcOH with Zn dust, which does not change solns. of **B**. Na-Hg in alc. likewise immediately produces the blue color. Comparison of the absorption spectra shows that the resulting blue soln. is identical with those of the "radical." This behavior towards Zn dust is entirely analogous to that of the HCl salt of  $\gamma,\gamma'$ -dipyridyl and as a matter of fact *N,N'*-dibenzyl-dipyridinium dichloride (**F**), easily obtained from dipyridyl and  $\text{PhCH}_2\text{Cl}$  at  $150^\circ$ , gives with Zn dust in org. solvents the same oxidizable blue soln. as **E** and yields in  $\text{H}_2\text{O}$  with KI a diiodide identical with **E**; the **E** from both sources yields the same perchlorate and hexanitrocobaltiate. The perchlorate also gives the blue color with Zn. **C** is therefore not **D** but a dipyridyl deriv., and if it is still to be considered as a "radical" it must be *N,N'*-dibenzyl- $\gamma,\gamma'$ -dipyridinium (**I**) and hence contain 1 atom H less for each pyridine nucleus; this would explain why O is necessary for its formation from **A** and why the solns. of the crystd. **C** do not at equil. again contain the colorless "dimer." The double ammonium formula (**I**) seems to fit the facts better than the alternative quinonoid formula (**II**), although the latter is not wholly excluded. How **C** is formed from **A** is difficult to explain. The easy oxidizing away of the two H atoms on the central C atoms is remarkable, as is also the cleavage between the nuclei (with formation of **B**) by oxidation with  $\text{AgNO}_3$ , an observation of Hofmann's which has been fully confirmed, while **C** gives only **F** with  $\text{AgNO}_3$ . As shown before and now confirmed beyond doubt, fresh solns. of **A** are not excessively oxidizable; only after warming, protected from the air, does it form brown-yellow solns. which, even after cooling completely, are immediately turned intensely blue by the air and again decolorized by an excess of air. If solns. freshly prepd. in the cold and protected from the air are treated with I, the I color disappears immediately and there is produced only a faint green color which again disappears on addition

of more I; the  $H_2O$ -sol. portion of the product is monomol. benzylpyridinium iodide with scarcely a trace of a dipyriddy compd. If, however, the I is dropped into a boiling soln. of A (protected from the air) there is obtained a deep blue soln. similar to that produced by air and decolorized only by further addition of I; the reaction is not smooth and quant. and the  $H_2O$ -sol. portion of the product contains both E and the monomol. iodide; E is formed only when the soln. has first been turned blue by the halogen, *i. e.*, its formation results from the production of C under the influence of the halogen. Emmert's interpretation of his results on the titration with I (C. A. 14, 2794) need revision in the light of the above results. It is also possible that the "*N*-benzylpyridinium" described in paper I is really a dimol. product. It has been found that Dimroth and Heene's "*N,N'*-diacetyl-tetrahydro- $\gamma,\gamma'$ -dipyridyl" (C. A. 16, 1591) likewise requires the presence of atm. O for its formation. To handle C, which darkens and becomes sticky in a few min. in the air, it is advisable at once to press it into tablets and keep it in  $CO_2$ . Mol. wt. detns. in freezing AcOH in the app. already described in air-free and dry H gave values ranging from 180 to 380 (av. 272). E seps. from MeOH in short red needles, m.  $232^\circ$ ; *hexanitrocollitate*, yellow, m.  $121-2^\circ$  (decompn.); *perchlorate*, fine needles from  $H_2O$ , m.  $257^\circ$ ; *chloroplatinate*, almost colorless; *dichloride* (F), finely cryst. mass. Very dil. solns. of C and of the dihalides reduced with Zn show a narrow absorption band in the middle red and the yellow is completely absent; in more concd. solns. the red disappears first in the longer and then also in the shorter wave-length region, the short wave-length blue persisting longest. Mineral acids quickly destroy C; it quickly dissolves in HCl-AcOH without turning blue and on evapn. to dryness and extn. with  $H_2O$ , F can be detected in abundance. Treated under MeOH in a  $CO_2$  atm. with NO it gives a light brown-yellow soln. which, when boiled a short time, becomes intensely blue and is decolorized on shaking with air.



**Constitution of picrorocelline, a diketopiperazine derivative from Rocella fuciformis.** M. O. FORSTER AND WM. B. SAVILL. *J. Chem. Soc.* 121, 816-27 (1922).—Picrorocelline (A) (Stenhouse and Groves, *Ann.* 185, 14) has the formula  $C_{30}H_{20}O_4N_2$  (not  $C_{27}H_{18}O_4N_2$ ), m.  $190-220^\circ$  according to the rate of heating, and has  $[\alpha]_D^{25} 12.5^\circ (0.9991 \text{ g. in } 25 \text{ cc. } CHCl_3)$ . *Dimethyl derivative* (A'),  $C_{28}H_{20}O_4N_2$ , lustrous, transparent elongated prisms, m.  $220^\circ$ . On reduction this yields *2,5-diketo-3,6-dibenzyl-1,4-dimethylpiperazine* (B), lustrous microplates, m.  $165^\circ$ , the constitution of which was established by the reduction of E. *Anhydronicrorocelline* (C),  $C_{28}H_{20}O_4N_2$ , results by heating A with 10% NaOH until the liberation of  $NH_3$  ceases, or by heating in small lots at  $180^\circ$  for 5-10 min., needles, m.  $155^\circ$ ,  $[\alpha]_D -463.7^\circ$ . *Methyl derivative* (C'), prisms, m.  $139^\circ$ ,  $[\alpha]_D -661.2^\circ$ . *Xanthorocelline* (*2,5-diketo-3,6-dibenzylidene-1-methylpiperazine*) (D),  $C_{18}H_{14}O_2N_2$ , results by further heating of C or by boiling A in glacial AcOH contg. a little HCl, long, faintly yellow, slender needles, m.  $184^\circ$ . The *methyl derivative* (E), formed by boiling A' with  $Ac_2O$  for 4 hrs., slender, faintly yellow needles, m.  $143^\circ$ ; it displays remarkable dimorphism, the needles changing in 24 hrs. to pale yellow, transparent rhomboidal prisms. The oxidation of D with  $HNO_3$  in AcOH gives  $BzH$ ,  $BzOH$  and  $p-O_2NC_6H_4CO_2H$ , together with 2,3,5,6-tetraketo-1-methylhexahydro-1,4-diazine (F) (Dubsky, C. A. 13, 2211), a conclusion confirmed by the absence of MeOH, HCHO and  $HCO_2H$  upon hydrolysis with NaOH and the formation of  $(CO_2H)_2$ ,  $NH_3$  and  $MeNH_2$ . The oxidation of E gave *2,3,5,6-tetraketo-1,4-dimethylpiperazine* (G), minute, lustrous, transparent rhomboidal plates, decomp. about  $360^\circ$ . C, oxidized with  $KMnO_4$  in

AcMe, gave 2,3,5-triketo-6- $\alpha$ -methoxybenzyl-1(or 4)-methylpiperazine, lustrous transparent 6-sided prisms, m. 206°,  $[\alpha]_D$  18.6°; hydrolysis with NaOH gave MeNH<sub>2</sub>, (CO<sub>2</sub>H)<sub>2</sub> and PhCH<sub>2</sub>COCO<sub>2</sub>H. C' gave 2,3,5-triketo-6- $\alpha$ -methoxybenzyl-1,4-dimethylpiperazine, spherical aggregates of needles or transparent, rhomboidal plates, m. 176°,  $[\alpha]_D$  -15.6°. On hydrolysis the same products were obtained as above. The action of PhNH<sub>2</sub> on F liberates NH<sub>3</sub> and gives (CONHPh)<sub>2</sub>, PhNHCOCOCONH<sub>2</sub> and a compd., possibly unsym. phenylmethyloxamide, pale, yellow needles, m. 174°. PhNH<sub>2</sub> and G likewise give (CONHPh)<sub>2</sub> and PhNHCOCOCONHMe, m. 187°. The constitution of E was established by methylation of 2,5-diketo-3,6-dibenzylidenepiperazine (Sasaki, C. A. 15, 2077). It seems probable that A is developed in the lichen by intramol. condensation of PhCH(OMe)CH(NHMe)CO<sub>2</sub>H and PhCH(OH)CH(NH<sub>2</sub>)CO<sub>2</sub>H or of the corresponding acids in which the N-Me group is transposed, and, with the exception of the position of the Me group, is represented by the formula,



This is the only one of 135 lichens which contains N.

C. J. WEST

Formation and hydrolysis of lactones (KAILAN) 2. Reaction kinetics of the influence of NH<sub>3</sub> on aromatic aldehydes (DOBLER) 2.

BRIELMAN, PAUL: (I) Über die Konstitution der Isocampholsäure. (II). Eine neue Aufspaltung des Cyclopentanringes. Basel: Buchdr. der National-Zeitung. 32 pp.

HOLLEMAN, A. F.: Lehrbuch der organischen Chemie für Studierende an Universitäten und Technischen Hochschulen. 16th Ed. revized. Berlin and Leipzig: Vereinigung Wissenschaftlicher Verleger W. de Gruyter & Co. M 60. Reviewed in Z. angew. Chem. 35, 236(1922).

Benzyl alcohol. R. E. NONTONNA. U. S. 1,416,859, May 23. Cl-free benzyl alc. is prepd. by combining crude benzyl alc. with CaCl<sub>2</sub>, breaking up the compd. thus formed by treatment with H<sub>2</sub>O and sepg. the benzyl alc. from the residue.

Anthraquinone. C. CONOVER and H. D. GIBBS. U. S. 1,417,367, May 23. Anthracene vapor is oxidized by mixing it with air and passing the mixt. over V oxide as a catalyst at a temp. of about 300-500° to produce anthraquinone.

Nitrophenols. T. L. DAVIS. U. S. 1,417,368, May 23. C<sub>6</sub>H<sub>5</sub> or toluene is treated with HNO<sub>3</sub> and Hg nitrate to produce a complex compd. and this compd. is treated with HNO<sub>3</sub> to form nitro compds.

Acetaldehyde. H. W. MATHESON. Can. 218,373, May 9, 1922. C<sub>2</sub>H<sub>2</sub> is passed through an acid soln. of not more than 6% concn. and contg. an oxide of Hg, maintained at a temp. of 60-66° and a pressure below 2 lbs. per sq. in. over atm. The process is made continuous by using an excess of C<sub>2</sub>H<sub>2</sub> at a temp. at which the CH<sub>3</sub>CHO distills off and adding water, acid and catalyst as required. Cf. C. A. 14, 288.

Urea from "lime-nitrogen." O. NYDEGGER and H. SCHELLENBERG. U. S. 1,417,277, May 23. "Lime-nitrogen" is treated with HNO<sub>3</sub> in the presence of a concd. soln. of Ca(NO<sub>3</sub>)<sub>2</sub>, which serves to moderate the reaction.

Guanidine. T. L. DAVIS. U. S. 1,417,369, May 23. Dicyanodiamide is hydrolyzed with NH<sub>3</sub> to form guanidine carbonate and the latter is treated with acids to form other salts.

## 11—BIOLOGICAL CHEMISTRY

PAUL E. HOWE

A—GENERAL

FRANK P. UNDERHILL

**The presence of amino acids in milk.** G. VIALE. *Biochim. e terapia sper.* 8, 321-4(1921).—N present as  $\text{NH}_3$  in the fresh milk was tested for by distn. at  $50^\circ$ , 30 mm. pressure. None was found in the samples examd. Amino N was detd. by the method of Van Slyke. For cow milk (fresh) the av. content of amino N is 8.6 mg. per 100 cc. The amino acids of milk (tryptophan, cystine) do not depend on the presence of a tryptic enzyme, but are secreted by the mammary glands. H. W. BANKS, 3RD

**Theoretical biology and a biologic conception of the world.** LEON ASHER. *Naturwissenschaften* 10, 473-7(1922).—A review and discussion of 2 works by Uexküll (cf. C. A. 15, 2457 and *Umwelt und Innenwelt der Tiere*, Berlin 1921). C. C. DAVIS

**Behavior of enzymes after drying and subjecting to heat. I. Enzymes of the enteric secretion.** CAMILLO ARTOM. *Arch. farm. sper.* 33, 1-6, 17-30, 33-7(1922).—The sucrose-inverting activity of the succus entericus of the dog is practically destroyed by heating 0.5 hour at  $60^\circ$ . The ereptic enzyme is more resistant to heat. Its activity is markedly diminished by heating 0.5 hour at  $60^\circ$  and destroyed at  $80^\circ$ . No difference was noted in either case whether fresh juice was employed or juice that had previously been exposed to the air for 48 hrs. When dried by a current of cold air and then redissolved in distd.  $\text{H}_2\text{O}$  succus entericus shows the same behavior toward heat as the fresh material. A. W. DOW

**The cellulose and amylase of the saliva of *Dixippus morosus*.** JAN BELEHRÁDEK. *Arch. intern. physiol.* 17, 260-5(1922).—The digestive fluid of *Dixippus morosus* contg. the product of the salivary glands is capable of dissolving cellulose and of transforming starch into sol. products. It has no action on fats or proteins. The amylolytic power is marked: Crude starch is attacked and iodized starch decolorized in a few seconds. An alk. medium is the most favorable for one amylase action: Acid retards but does not inhibit entirely. Although starch is rapidly dissolved and loses the  $\text{I}_2$  coloration capacity, the presence of reducing sugars cannot be detected for some time after and only in alk. medium. F. S. HAMMETT

**Surface activity and the toxicity of the saponins.** I. KOFLER. *Biochem. Z.* 129, 64-72(1922).—Using the concn. of saponin which is just sufficient to kill small roaches (fish) of 0.1 to 0.5 g. wt. in an hr., and the concn. of the drug which is just sufficient to hemolyze a 2% suspension of defibrinated human placenta blood in physiol. NaCl soln. as indices, K. found that there is no relation between these values and the surface tension detd. stalagmometrically. The various saponins used arrange themselves into series of different distributions according to the concns. used when considered from the point of view of the lowering of surface tension. When curves are plotted in which the ordinates are surface tension values and the concns. of saponins are abscissas, the curves of the different saponins cross. The toxicity does not follow the curves, it is independent of the concn. and in a comparison of 2 saponins, before and after the point of crossing, does not follow the expected values according to the theory of partial pressure. It is, therefore, evident that a detn. of the surface tension lowering caused by these compds. is not a good index of their biol. action. F. S. HAMMETT

**Metacholesterol and its related products. III.** I. LIFSCHÜTZ. *Biochem. Z.* 129, 115-27(1922).—Metacholesterol was prepd. in the wet way from 1 g. cholesterol by warming with 1 g. benzoyl peroxide in 50 cc. abs. alc. for 1 hr. To the mixt. there was added 1 cc. of 50% KOH and the whole was warmed for 10 mins., then dild. with an equal vol. of  $\text{H}_2\text{O}$  and extd. with  $\text{Et}_2\text{O}$  by shaking. The neutral washed  $\text{Et}_2\text{O}$  ext. was freed from



H<sub>2</sub>O on the H<sub>2</sub>O bath. On the appearance of turbidity just that amt. of alc. was added to clarify and the soln. was allowed to cool and crystallize. The product when filtered off, washed with 90% alc. and dried yielded some 75 to 80% of the expected amt. The hygroscopicity of metacholesterol in mixts. of fats which do not take up H<sub>2</sub>O is its most characteristic property and can be used as a test for its presence. The compd. can be prepd. in the dry way by heating rhombic cholesterol on the oil-bath at 148 to 150° for 35 to 40 min. The cryst. mass which seps. on cooling is dissolved in hot 90% alc. from which metacholesterol crystallizes out. Oxycholesterol is recoverable from the filtrates of both processes. Metacholesterol was also prepd. by the action of radiant energy on cholesterol. The bromide m. 101–106° while the bromide of cholesterol m. 93–94°. The mean of 4 mol. wt. detns. gave 369 for metacholesterol. Hence it is probable that it is an isomer of rhombic cholesterol. Its optical activity is  $[\alpha]_D = 33.7^\circ$ .

F. S. HAMMETT

**Regeneration of diastase and its dependence on oxygen.** W. BIEDERMANN. *Biochem. Z.* 129, 582–93(1922).—In 10 cc. clear filtrate from a very active saliva heated on a water-bath to 100° a turbidity occurs at about 73°, which soon changes to a slight flocculation at about 80° because of coagulation of proteins. When portions of this turbid mixt. are incubated with aerated starch soln. at 45° digestion takes place rapidly. When portions are incubated with O-free starch soln. the I<sub>2</sub> test is clearly given after several hrs. The clear filtrate from the turbid mixt. shows a delayed digestion on the oxygenated starch and no action on the O-free starch soln. This phenomenon is considered as evidence of a regeneration of the diastatic power of the saliva which had been diminished by heating. The finely divided coagulated protein also plays a significant part. Further evidence is given which leads to the idea that O is combined with the enzyme or enzyme residue in the natural state and that this union is destroyed by boiling, thus inhibiting the enzyme activity.

F. S. HAMMETT

**The effects of various salts on the outgrowth from experimental amebocyte tissue near the isoelectric point and with the addition of acid or alkali.** LEO LOEB and K. C. BLANCHARD. *Am. J. Physiol.* 60, 277–307(1922).—At the isoelec. point amebocytes of limulus are least resistant to injurious influences and have the greatest permeability to the surrounding fluid. Acid, and to some extent alkali, may protect the cells not only in isotonic but in certain cases also in hypotonic and hypertonic solns. Under the influence of acid in optimal concn. the cells, their consistency, the character of pseudopods and the movement of granulooplasm remain healthy. J. F. LYMAN

**Physical chemistry of color vision.** FRITZ WEIGERT. *Z. physik. Chem.* 100, 537–65(1922).—Extensive photochem. expts. upon the sp. changes in the perceptive elements of the retina under influence of light. These changes through their qual. and quant. relations give rise to definite and const. sensory impressions of light intensity and color. The theory proposed by W. places all visual changes in the visual purple system in opposition to Hering's theory (cf. *C. A.* 15, 1839, 3939). W. A. P.

**Does the kinetics of trypsin depend on the formation of a compound between enzyme and substrate?** J. H. NORTHROP. *J. Gen. Physiol.* 4, 487–509(1922).—The velocity of hydrolysis of gelatin and casein by trypsin increases more slowly than the substrate concn. and finally becomes nearly independent of it. It is also independent of the viscosity of the soln. The relative velocity of hydrolysis of any 2 substrate concns. is independent of the quantity of enzyme used. The % retardation of the rate of hydrolysis by inhibiting substances is independent of the substrate concn. Expts. show that the enzyme and the inhibiting reaction products (cf. *C. A.* 16, 1589) combine to form a widely dissociated compd. The enzyme does not combine with the substrate, as shown by the fact that an increase in substrate concn. does not affect the equil. between enzyme and inhibitor. The rate of digestion of a mixt. of casein and gelatin

equals the sum of the rates of hydrolysis of these 2 substances alone, indicating that the rate is proportional to the concn. of free enzyme. When the reaction is followed by detg. the change in substrate concn., the rate of digestion is found to be proportional to the substrate concn., *i. e.*, it follows the law of mass action. C. H. R.

**Studies on the regulation of osmotic pressure. II. The effect of increasing concentrations of albumin on the conductivity of a sodium chloride solution.** W. W. PALMER, D. W. ATCHLEY AND R. F. LOEB. *J. Gen. Physiol.* **4**, 585-9(1922); cf. *C. A.* **15**, 3501.—Cryst. egg albumin dialyzed till practically salt-free was brought to  $p_H$  3.1, 5.3 and 7.3, resp., with NaOH or HCl and used in 1.1-8.3% solns. H-ion concn. was detd. by the gas-chain method, cond. by the Kohlrausch bridge at 25°. An increase in cond. with increasing concn. of albumin is shown to be greatest at  $p_H$  3.1, least at 5.3 which is near the isoelec. point of the protein. Gradually increasing amts. of albumin were then added to 0.6% NaCl soln. at  $p_H$  3.5, 5.0 and 7.3, resp. At  $p_H$  3.5 cond. increases with increase in albumin concn., but at  $p_H$  5.0 and 7.3 there is a decrease with increased concn. of albumin. These results indicate that egg albumin influences the cond. of a NaCl soln. in the same manner as gelatin. (Cf. *C. A.* **15**, 3501.) The factor detg. the influence of protein on the cond. of a NaCl soln. is probably the degree of ionization which depends on the  $p_H$  of the soln. At the H-ion concn. of blood, egg albumin is so slightly ionized that it decreases the cond. of the salt soln. by mech. interference of the undissociated albumin mols. CHAS. H. RICHARDSON

**The elimination of discrepancies between observed and calculated potential difference of protein solutions near the isoelectric point with the aid of buffer solutions.** JACQUES LOEB. *J. Gen. Physiol.* **4**, 617-9(1922).—It was previously noted (*C. A.* **15**, 2455; **16**, 1597) that the p. d. between a soln. of gelatin or albumin chloride inside a collodion membrane and an outside soln. free from protein could be calcd. from the difference in H-ion concn. between inside and outside solns. The agreement of the observed and calcd. values was perfect when the soln. contained a neutral salt or when its  $p_H$  was not close to the isoelec. point of the protein. At a  $p_H$  near 4.7, agreement was not perfect. The use of Na acetate-acetic acid buffer solns. between  $p_H$  4.65 and 3.34 gave exptl. results in very close accord with the calcd. p. d., indicating that the discrepancy lay in the uncertainty of the  $p_H$  measurements of the outside aq. soln. near the isoelec. point. These results show that the observed p. d. and the p. d. calcd. on the basis of Donnan's theory of the p. d. between membrane equilibria are the same. CHAS. H. RICHARDSON

**Electrical charges of colloidal particles and anomalous osmosis. II. Influence of the radius of the ion.** JACQUES LOEB. *J. Gen. Physiol.* **4**, 621-7(1922); cf. *C. A.* **14**, 2573; **16**, 1786.—Solns. of KCl, NaCl, and LiCl were sepd. from H<sub>2</sub>O by a collodion-gelatin membrane; the  $p_H$  of the salt solns. and H<sub>2</sub>O were on the acid side of the isoelec. point of the gelatin. Under these conditions water diffused from the side contg. pure H<sub>2</sub>O into the salt solns., the rate increasing inversely with the radius of the cation. This influence of the cations is not due to a difference in p. d. between the liquid and membrane inside the pores of the gelatin film of the collodion membrane. The p. d. across the membrane, however, was affected by the 3 cations in a way similar to the transport of water through the membrane. Since the p. d. across the membrane varies inversely as the relative mobility of the 3 ions in question, it is suggested that the influence of these cations on the diffusion of a liquid through a membrane is partly at least due to a diffusion potential. CHAS. H. RICHARDSON

**The colloidal behavior of edestin.** D. I. HITCHCOCK. *J. Gen. Physiol.* **4**, 597-615(1922).—Edestin when prepd. from hemp seed by the method of Osborne (*J. Am. Chem. Soc.* **24**, 28, 39(1902); Abderhalden's "Handb. biochem. Arbeitsmethoden" 1910, II, 289) is amphoteric electrolyte reacting stoichiometrically with acids and bases.

A p. d. is developed when a soln. of edestin chloride or acetate is sepd. by a collodion membrane from a protein-free acid soln. The p. d. is influenced by salt and H-ion concns. as predicted by Donnan's theory of membrane equil. The osmotic pressure is affected by salt and H-ion concns. in the same way as the p. d. The colloidal behavior of edestin is analogous to that of gelatin, casein and egg albumin as observed by Loeb. (Cf. Loeb, "Proteins and the Theory of Colloidal Behavior," N.Y. and London, 1922.)

CHAS. H. RICHARDSON

**Alterations in the charge of cells, cell components, and membranes.** KARL HÄRSCH. *Arch. ges. Physiol.* (Pflüger's) **190**, 198-211(1921).—Negatively charged cell components, starch granules, cellulose, agar, gum, lecithin, cholesterol, vegetable oil, and albumin suspended in sugar-saline solns. contg. La ions became discharged or suffered a reversal of charge. With the gum and agar the La concn. was 0.1 *M*, with the albumin it was 0.001 *M* and with the other substances the concns. were between 0.01 and 0.02 *M*. Yeast cells and lycopodium spores reacted at about 0.02 *M*, while washed animal cells, leucocytes and erythrocytes, changed at 0.1 *M*. Histone sulfate, clupeine sulfate, and salts of the color bases (neutral red, Rhodamine S, methyl violet) also caused alterations in the charge. Alkaloid salts (cocaine-HCl, morphine-HCl, quinine-H<sub>2</sub>SO<sub>4</sub>, and optochin-HCl) were inert. The presence of certain substances in the fluid may alter the effectiveness of the La ions; albumin and gelatin exert a sensitizing influence, gum and agar diminish the effect. Lecithin sensitizes better than cholesterol. Membranes can be discharged in a similar manner: Pig bladder, muscle membranes, parchment paper, and agar membranes are all subject to a change in charge by La(NO<sub>3</sub>)<sub>3</sub>, by histone and clupeine sulfates and by Rhodamine S.

G. H. S.

**Protein derivatives of a basic nature.** K. FELIX. *Z. physiol. Chem.* **116**, 150-65 (1921).—From the intestinal mucosa and from lymph glands substances were isolated having their hexone base N divided as follows: arginine N 26% and 14%, histidine N 11% and 3% (?), lysine N 17% and 27%. The characteristic properties of both substances are: strongly alk. reaction, non-precipitability with NH<sub>3</sub>, K<sub>4</sub>Fe(CN)<sub>6</sub>, Witte peptone and nucleic acid, red-violet biuret, and resistance to tryptic digestion. They therefore differ from both protamines and histones.

R. L. STEHLE

**Enzymic synthesis of fructose-zymophosphate.** H. v. EULER and F. NORDLUND. *Z. physiol. Chem.* **116**, 220-14(1921).—The rate at which phosphate is removed from a sugar-yeast system is greatest when  $p_H = 6.4$ . This is within the limits of the most favorable reaction for CO<sub>2</sub> production but considerably removed from the optimum reaction for invertase action ( $p_H = 4$ ). The coenzyme of yeast has little effect on the process.

R. L. STEHLE

**Desaminoproteins.** J. HERZIG and H. LIEB. *Z. physiol. Chem.* **117**, 1-12(1921).—The Van Slyke and Sørensen amino-N methods when applied to glutin, ovalbumin, casein and gliadin and their desamino derivs. gave the same results for each pair of compds.

R. L. STEHLE

**Chemistry of homogentisic acid. II. Behavior toward ferric chloride on boiling.** C. TH. MÖRNER. *Z. physiol. Chem.* **117**, 67-84(1921).—The largest yield of "quinone substance" was obtained by using 33 g. homogentisic acid (added after boiling had begun), 400 cc. 37.5% FeCl<sub>3</sub> soln. in a 700 cc. flask and collecting 100 cc. of distillate. The formation of the "quinone substance" soon ceases, owing to the production of FeCl<sub>3</sub> and HCl, the actions of which are inhibitory. Homogentisic acid, lactose, benzoylhydroquinone, arbutin, toluylhydroquinone and gentisic acid gave no "quinone substance" on distn. as above. The statement to be found in the literature that homogentisic acid on heating with FeCl<sub>3</sub> soln. gives the odor of quinone could not be substantiated. **III.** *Ibid* **117**, 85-90(1921). An unusually good prepn. of homogen-

tistic acid having been obtained M. describes it in detail. Monoclinic crystals of prismatic habit, elongated perpendicularly to the plane of symmetry. Faces in zone of the *b* axis, with the exception of (100), streaked.  $(100):(001) = 76^\circ 10'$ . Of the remaining faces only (010) could be defined crystallographically. Extinction angle for Na light on (100) =  $10^\circ 20'$ . The compd. is not converted into a lactone by heating at  $100^\circ$  as stated by Wolkow and Baumann (*Z. physiol. Chem.* 15, 228(1891)) nor does it sublime. It is sol. in 1.8 parts of water.

R. L. STEHLÉ

**The role of vitamins in the chemistry of the cell.** W. R. HESS. *Z. physiol. Chem.* 117, 284–308(1921).—The condition which develops in pigeons as the result of a vitamin-free diet is due to the depletion of the respiration enzymes of the tissues. The pathol. picture of pigeon beriberi can be reproduced by means of HCN which inhibits tissue respiration. As a measure of the changes in the oxidizing capacity of the various tissues the capacity to reduce *m*-nitrobenzene was estd.

R. L. STEHLÉ

**A conjugated nucleic acid from the pancreas.** II. E. HAMMARSTEN AND E. JORPES. *Z. physiol. Chem.* 118, 224–32(1922).—The nucleic acid isolated by H. (*C. A.* 15, 1730) from the pancreas contains guanylic acid and a substance contg. a pentose and adenine.

R. L. STEHLÉ

**Lehrbuch der physiologischen Chemie.** Edited by S. G. Hedín, Olof Hammarsten, J. E. Johanson, and T. Thunberg. 9th Revised ed. München & Wiesbaden: J. F. Bergmann. 830 pp. M 144.

Significance of the second dissociation constant of uric acid for the equilibrium of monourate solutions (KANITZ) 2. The sol-gel equilibrium in protein systems (BOGUE) 2. A quantitative study of the adsorption in solution and at interfaces of sugars, etc. (CLARK, MANN) 2.

BURNS, D.: **An Introduction to Biophysics.** London: J. & A. Churchill. 435 pp. 21s. Reviewed in *Nature* 109, 704(1922).

HANDOVSKY, H.: **Leitfaden der Kolloidchemie für Biologen und Mediziner. Mit einem Anhang über die Anwendbarkeit kolloid-chemischer Erfahrungen zur Aufklärung biologischer Probleme.** Dresden: Th. Steinkopf. M 45.

## B—METHODS AND APPARATUS

STANLEY R. BENEDICT

**The determination of the relative number of red blood cells of different resistances (osmotic resistance curve) by means of sodium sulfate.** The influence of nutrition on the resistance and regeneration in hemorrhagic anemia. H. J. HAMBURGER. *Biochem. Z.* 129, 163–82(1922); cf. *C. A.* 16, 941.—An isotonic soln. of  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  (3%) when neutralized if necessary with 5%  $\text{NaHCO}_3$  is quite suitable not only for washing but also for the detn. of the relative no. of red cells of different resistances. Deplasmation is effected by washing the cells 2 or 3 times with the soln. This also removes the adsorbed lecithin membrane. The curve of resistance to varying concns. of  $\text{Na}_2\text{SO}_4$  made by corpuscles so treated is the "primary resistance curve." The unwashed cells which have the lecithin envelope give the so-called "secondary resistance" curve. Washing with  $\text{Na}_2\text{SO}_4$  makes the cells more resistant. This indicates that lecithin lowers the erythrocyte resistance. Pure NaCl solns. are not capable of yielding satisfactory results in differential resistance studies. This is largely attributable to the lyotropic influence, which can be neutralized by the addition of a detd. amt. of Ca ions. The use of equilibrated salt solns. is not for unskilled experimenters. The difficulty is obviated by the use of  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  solns. With such a soln. it was found that lecithin and fat-contg. foods are necessary for blood regeneration after hemorrhagic anemia in rabbits. The use of  $\text{Na}_2\text{SO}_4$  also provides a simple method of detg. whether the change in resistance arises from the blood cells, the plasma or both. F. S. HAMMETT

The determination of uric acid in blood. S. R. BENEDICT. *J. Biol. Chem.* **51**, 187-207 (1922).—The new method is more expeditious and simpler than the Folin and Wu pptn.-decompn. method and is far safer for most analysts. The new reagent is much more sp. and yields nearly 7 times as much color from a given wt. of uric acid. The process is recommended only for application to the Folin-Wu filtrates from human blood; its application to other bloods and to the detn. of uric acid in urine is under investigation. *Method*.—Ppt. the blood with  $\text{H}_2\text{WO}_4$  as described by Folin and Wu, allowing the pptd. mixt. to stand for at least 10 min. before filtering to insure complete protein pptn. Excess of K salts is undesirable in the detn. and  $\text{Na}_2\text{C}_2\text{O}_4$  may be used to advantage instead of the K salt to prevent coagulation. Transfer 5 cc. of the water-clear filtrate (representing 0.5 cc. of blood) to a test-tube (these need not be graduated but should be of uniform diam., 18 to 20 mm.) and add 5 cc. of  $\text{H}_2\text{O}$ . Place 5 cc. of the standard uric acid soln., contg. 0.02 mg. of uric acid, in another test-tube and add 5 cc. of  $\text{H}_2\text{O}$ . To both standard and unknown add 4 cc. of 5% NaCN soln. contg. 2 cc. of concd.  $\text{NH}_4\text{OH}$  per l. (measure this *always* from a buret on account of the high toxicity of the NaCN). To each tube then add 1 cc. of the As phosphotungstic acid reagent. Mix by one inversion immediately after adding the reagent, place the tubes in boiling water at once and allow them to remain there for 3 min. after the immersion of the last tube. The time elapsing between the immersion of the 1st and last tubes should not exceed 1 min. and therefore not more than 4 unknowns should be run in one series. Remove the tubes and place them in a large beaker of cold  $\text{H}_2\text{O}$  for 3 min. Read in a colorimeter against the standard within 5 min. With the 0.02 mg. standard, the results are exact when the unknown reads between 10 and 24 mm. with the standard set at 15 mm., thus covering a range of from 2.5 to 6 mg. of uric acid per 100 cc. of blood. With the few bloods falling outside these limits the detns. should be repeated. With those contg. more than 6 mg., less of the blood filtrate should be used with more  $\text{H}_2\text{O}$  to make the vol. 10 cc. before adding the reagents. With those contg. less than 2 mg., 5 cc. of the filtrate should be employed and 0.01 mg. of uric acid should be used in the standard. It is not satisfactory to change the diln. of either the standard or unknown after the reaction is completed. *Calc.*: (Reading of standard/reading of unknown)  $\times$  4 = mg. of uric acid per 100 cc. of blood. "*Ultra-micro*" method for use where blood must be obtained by puncture: Carefully pipet 0.2 cc. of blood into a narrow pointed centrifuge tube, add 1.4 cc. of  $\text{H}_2\text{O}$  and stir the mixt. with a fine glass rod. Add 0.2 cc. of 10%  $\text{Na}_2\text{WO}_4$  soln. and 0.2 cc. of 0.75 *N*  $\text{H}_2\text{SO}_4$ , stir thoroughly and allow to stand for 10 min. Centrifuge at high speed for a few min. Pipet 1 cc. of the clear supernatant liquid into a long narrow (1 cm.) test-tube. Add 1.8 cc. of 2.8% NaCN soln. (contg. 1.5 cc. of concd.  $\text{NH}_4\text{OH}$  per l.) and 4 drops (0.2 cc.) of the As phosphotungstic acid reagent. Treat the mixt. as the unknown is treated in the regular process and compare with the 0.02 mg. regular standard soln. The 3 cc. of colored soln. can be readily read in the narrow form cup of the Bock-Benedict colorimeter up to a height of about 24 cm. It is naturally essential that calibrated pipets be used and that all measurements be made with great care. *Reagents*: As phosphotungstic acid.—Dissolve 100 g. of pure  $\text{Na}_2\text{WO}_4$  in 600 cc. of  $\text{H}_2\text{O}$  in a l. flask, add 50 g. of pure  $\text{As}_2\text{O}_3$ , 25 cc. of 85%  $\text{H}_3\text{PO}_4$  and 20 cc. of concd. HCl; boil for 20 min., cool and dil. to 1 l. The reagent appears to keep indefinitely. The NaCN soln. should be prepd. fresh once in 2 months. *Standard uric acid solns.* The standard solns. employed have a concn. of uric acid considerably below the soly. of pure uric acid in  $\text{H}_2\text{O}$  and are prepd. once in 2 weeks by appropriate diln. of the phosphate standard of Benedict and Hitchcock (*C. A.* **9**, 1626) which may be relied upon to keep about 2 months. It is well to keep two standards on hand. Prep. the one most frequently used, which contains 0.02 mg. of uric acid in 5 cc., by measuring 10 cc. of the phosphate standard soln. into a 500-cc. volumetric flask half filled with distd.  $\text{H}_2\text{O}$ . Add 25 cc. of dil. HCl (1:10) and dil. to the mark. The 2nd

standard contains 0.01 mg. per cc. and is prepd. in the same way except that 25 cc. of the phosphate standard is used. The new method tends to give higher results than the Folin-Wu procedure but in the analysis of 50 samples of blood there was no case in which the amt. obtained by the new method exceeded the old by as much as 2 mg. of uric acid per 100 cc. of blood. The difference chiefly affects those bloods with which the Folin-Wu method gives a figure of 2.5 mg. or below. "Where the new process is used it is probable that the commonly accepted figures should be increased by about 0.5 mg. per 100 cc. so that the usual normal figures would probably be about 3.0 mg. and no evidence of definite uric acid retention would be evident until a figure of 4.0 mg. or over is reached."

A. P. LOTHROP

**Reduction of the aromatic nitro group as an indicator of respiratory and fermentative processes. A method for the comparative quantitative estimation of biologic oxido-reduction. I. Cell respiration.** W. LIPSCHITZ AND A. GOTTSCHALK. *Arch. ges. Physiol.* (Pflüger's) 191, 1-32(1921).—A colorimetric method for detg. the respiratory activity (and fermentative activity as well) of cells is described, based upon the reduction of *m*-dinitrobenzene to *m*-nitrophenylhydroxylamine. Finely minced tissue in water is combined with *m*-dinitrobenzene and after repeated shaking the filtrate is examd. colorimetrically for the *m*-nitrophenylhydroxylamine, thus showing the extent of the biol. H<sup>+</sup> activation. With frog muscle tissue the reduction is detd. by the presence of, and is dependent upon, the concn. of the coenzyme (Meyerhof) and the time curve for the reduction corresponds with the time curve for the respiration. The reduction is thermolabile, being entirely inhibited at temps. above 80°. This indicates that the process is associated with an intact cell structure. There is an optimum O pressure for the reduction and deviations from this value impair the reaction. Narcotics are inhibitive and with certain combinations of them summation effects are noted. Ordinary narcotics combined with HCN fail to show additive effects, indeed, there is somewhat less action than would be expected from adding the sep. effects of each compd. Unlike the curve of inhibition of respiration, that indicating the inhibition in reduction rate brought about by HCN consists of two phases. Aq. exts. of muscle show no reduction but if extd. muscle is combined with muscle ext. or with yeast juice, or even with succinic, fumaric, citric, glutamic, or  $\alpha$ -glycero-phosphoric acids it is restored. Lactic acid will restore the activity after a partial extn. The addition of such compds. as malic, glutaric, pyruvic, hydroxybutyric, and tartaric acids, glycerol, glyceric acid, glucose, levulose, and glycogen will not restore the activity. Succinic and fumaric acids intensify, malic acid and saponin inhibit, the reduction of fresh non-extd. muscle.

**II. Cell fermentation.** *Ibid* 33-50.—The muscle cells of *Ascaris megalocephala* reduce *m*-dinitrobenzene, the reduction being thermolabile, dependent upon a coenzyme, but not of necessity associated with intact cells. O does not inhibit the reaction; inhibition by narcotics is proportional to their concn. HCN in increasing concn. inhibits up to 30% of the activity, giving an inhibition curve without particular significance and without evidence of diphasic character. *Lumbricus* cells, if intact, give a similar but less powerful reduction. The activity is inhibited up to 80% by HCN. O does not completely suppress the activity; narcotics are inhibitory. Bacterial cells, *B. proteus* and *B. butyricus* reduce the compd., the reduction being only incompletely inhibited by HCN.

G. H. S.

**The analytical isolation and differentiation of acetaldehyde, aldol and glyoxylic acid, as well as their occurrence in diabetic urine.** R. FRICKE. *Z. physiol. Chem.* 116, 129-49(1921).—Aldol is present in diabetic urine. It was identified by means of the compd. which, its deriv., crotonic aldehyde, forms with dimethylhydroresorcinol (dimedon). The deriv. of aldol with the same reagent (aldolmedon) m. 170-2°. The presence of glyoxylic acid and AcH in diabetic urine was confirmed.

R. L. STEHLE

Further details on the use of the "silver method" for the determination of acetaldehyde, its suitability for determining other aldehydes and a convenient method for removing acetaldehyde and other volatile substances from body fluids. R. PRICKE. *Z. physiol. Chem.* 118, 241-6 (1922).—Before heating, the soln. in the flask should be 1.5-2.0 fingers deep. It is brought to boiling, the flame removed for 5 min. and heating then resumed for 1 min. After cooling  $\text{NH}_3$  is added until the odor is strong. In washing the ppt. strong  $\text{NH}_3$  should be used, it having first been employed to rinse the flask. If the  $\text{AcH}$  is present in very small concn. colloidal  $\text{Ag}$  may form which cannot be filtered. In this case the  $\text{AcH}$  is concd. by steam distn. A quantity of distillate equal to 0.1 of the original soln. should be collected. The method is applicable to all water-sol. aldehydes. It has been used successfully with crotonic aldehyde and with aldol. The latter gives two mols. of  $\text{AcH}$ . R. L. STEHLÉ

The determination of purine bases in urine. H. STEUDEL AND SUNG-SHENG CHOU. *Z. physiol. Chem.* 116, 223-5 (1921).—Results obtained by the Krüger and Schmidt method may be 34% too high because of contamination with  $\text{NH}_4$  salts. This error may be eliminated by boiling the final ppt. with  $\text{MgO}$  before detg. the N content. R. L. STEHLÉ

The quantitative determination of tannase. K. FREUDENBERG AND E. VOLLBRECHT. *Z. physiol. Chem.* 116, 277-92 (1921).—See *C. A.* 16, 851. R. L. S.

The detection of small amounts of lead in urine. O. SCHUMM. *Z. physiol. Chem.* 118, 189-214 (1922).—In strong  $\text{HNO}_3$  soln. 0.3-0.1 mg. of  $\text{Pb}(\text{NO}_3)_2$  may be pptd. electrolytically with small Pt foil electrodes and 4 v. Pptn. occurs on both electrodes.  $\text{NaCl}$  and  $\text{KCl}$  interfere so that electrolysis must be continued until all the  $\text{Cl}$  has disappeared. Urine ashed with  $\text{HNO}_3$  and with  $\text{HCl}$  and  $\text{KClO}_3$  or urine contg. protein does not give satisfactory results. The addition of  $\text{CuSO}_4$  to the urine before pptg. with  $\text{H}_2\text{S}$  (the  $\text{Cu}$  serves to improve the filterability of the  $\text{PbS}$ ) and subsequent electrolysis of the concd.  $\text{HNO}_3$  soln. of the sulfides gave very satisfactory results. Four v. and 0.5 amp. were used; electrolysis lasted 16-20 hrs. For 1.5 l. of normal urine 15 cc. 25%  $\text{HNO}_3$  and 0.4 g.  $\text{CuSO}_4$  were employed and at the start the  $\text{H}_2\text{S}$  was passed in at room temp., then at 40-50° for  $\frac{1}{4}$  hr. R. L. STEHLÉ

Determining activity of invertase (HARDING) 28. The refractometer and the interferometer (HIRSCH) 12.

BECHER, SIEGFRIED: Untersuchungen über Echtfärbung der Zellkerne mit künstlichen Beizenfarbstoffen und die Theorie des histologischen Färbeprozesses mit gelösten Lacken. Berlin: Gebr. Borntraeger. M 75.

DENIGES, G.: Determination rapide des concretions et sables urinaires. Paris: Vigot frères. 12 pp. Fr. 1.50.

## C—BACTERIOLOGY

A. K. BALLS

Studies on the antiseptic action of acrolein. ALBERT BERTHELOT. *Rev. hyg.* 44, 16-19 (1922).—Expts. on *B. coli*, *B. mesentericus vulgaris*, *B. subtilis*, and *Staph. aureus* with acrolein (stabilized by the addn. of 0.2% pyrocatechol) to det. its germicidal and inhibitory powers in aq. soln. and as a vapor. It is inferior to  $\text{HCHO}$  in its action.

JACK J. HINMAN, JR.

The utilization of dextrose by the tubercle bacillus. C. J. GAMBLE AND MARGARET C. HERRICK. *Am. Rev. Tuberculosis* 6, 44-50 (1922).—Five strains of *B. tuberculosis*, 2 human, 2 bovine, and 1 avian, consumed dextrose from a liquid medium of 2% dextrose and 0.8% dehydrated broth to the extent of from 12% to 80%, (130 to 900 mg.) of the amt. originally present (50 cc.) when detd. by the Folin colorimetric method for blood sugar (*C. A.* 13, 2541; 14, 2353) slightly modified. The amt. consumed runs

closely parallel to the amt. of growth recorded. No differences in the rate of consumption of dextrose by the different strains were detected.

H. J. CORPER

**The use of salts and sugar in the preparation of dry typhoid vaccine.** S. CHIBA. *Centr. Bakt. Parasitenk., Abt. I* **88**, 76-9(1922).—The technic used is as follows: One cc. of a 10% soln. of the various substances to be tested was mixed with 0.1 g. typhoid bacilli and heated to 55° for 2 hrs. in a drying oven. It was then spread on flat dishes in a desiccator for 1 day. Of all the substances tested  $\text{CaCl}_2$  and Na citrate were the best for the purpose. A dried vaccine prepd. with them showed scarcely no decrease in antigenic property in 2 yrs. When dried with dextrose the prepn. can be used in agglutination tests. The method can be applied equally well to other bacteria.

JULIAN H. LEWIS

**The chemical properties of bacterial capsules.** EUGEN KRAMAR. *Centr. Bakt. Parasitenk., Abt. I* **88**, 401-6(1922).—The capsule of the pneumobacillus of Friedländer consists of galactan, a polymerized carbohydrate which yields galactose on inversion. The capsule of the anthrax bacillus is protein-like. Since it is P-free but contains S and yields a carbohydrate on hydrolysis it can be called a glucoprotein. The capsule from a bacillus isolated from rosy wine is so similar to that of anthrax that a relation is presumed. The capsule of *B. radicola* consists of a polymerized carbohydrate which yields dextrose on hydrolysis and therefore can be designated as dextran.

JULIAN H. LEWIS

**Preparation of culture media from yeast extract and yeast peptone.** J. KISTER. *Centr. Bakt. Parasitenk., Abt. I* **88**, 477-80(1922).—Yeast ext. is substituted for meat ext. and yeast peptone for Witte peptone in prep. culture media.

J. H. L.

**The fermentation reactions of certain streptococci. XLII. Studies in bacteria metabolism.** A. I. KENDALL, A. A. DAY, A. W. WALKER, AND MARJORIE RYAN. *J. Infectious Diseases* **25**, 189-206(1919).—Carbohydrates are important in bacterial nutrition chiefly as sources of energy. They spare or protect nitrogenous constituents in as far as energy requirements are concerned, but they do not and cannot substitute for nitrogenous substances, which are indispensable for the structural requirements of the organisms. It is probable that certain members of the group also become integral parts of structural units, as for example, components of nucleins. The significance of a classification of bacteria based on fermentation reactions depends on a recognition of the relation between the space arrangement of the carbohydrate and a fundamental capacity of the cytoplasm of the microbe to dissociate it with the liberation of energy for the cell. The products of fermentation produced by a great majority of bacteria are qualitatively very similar, irrespective of the carbohydrate fermented and of the organism inciting the process. The specificity of action of these bacteria would appear to depend principally on the products arising from the utilization of protein, not only for structure but for energy as well. The classification of bacteria, including streptococci, therefore, on the basis of fermentation reactions makes it possible to sep. them into convenient and distinct groups which have divisional value. There is no clearly discernible relationship, however, between cultural groupings based on carbohydrateolysis and pathogenesis.

JULIAN H. LEWIS

**Acid production by Streptococcus viridans in mediums of different hydrogen-ion concentration.** LINWOOD G. GRACE AND FLORENCE HIGHERGER. *J. Infectious Diseases* **26**, 451-6(1920).—A broth given an initial reaction of  $pH$  6.8 will favor a more rapid growth, while a broth having a reaction more alkaline than  $pH$  7.6 will distinctly retard growth. Among the 5% ascites, 0.2% glucose broth and the 1% glucose broth there appears to be no appreciable difference when growing in pure culture.

JULIAN H. LEWIS

**Studies on the biochemistry and chemotherapy of tuberculosis. XXII. The**



inhibitory action of certain organic mercury compounds on the growth of human tubercle bacilli. LYDIA M. DEWITT. *J. Infectious Diseases* 30, 363-71(1922).—The org. compds. of Hg are the most promising in the chemotherapy of tuberculosis. The present paper is a report of a series of these compds. on the growth of the tubercle bacillus. Most of the preps. were made by collaborating chemists; they include Hg compds. of phenol, nitro- and nitrosophenols, saligenin or phenolcarbinol, aniline, the nitro-anilines, methyl- and ethylanilines and nitroanilines. The power of phenol to inhibit the growth of the human tubercle bacillus is greatly increased by the substitution of a Hg salt in place of one atom of H; hence Hg united by 1 bond to C. It is also increased by the substitution of 1 NO<sub>2</sub> group for 1 H in the ring. The position of the NO<sub>2</sub> group has much to do with the degree of increase of the inhibitory power, the ortho position being most favorable and the para position next. This is probably due to a quinonoid change in the phenol nucleus. The position of the Hg group has also much influence on the degree of increase of inhibitory power, the ortho position seeming most favorable. The Hg bridge compds. seem also to have a high inhibitory power, at least in the 2 compds. tested, in both of which the bridge occupies the ortho position. Although saligenin or phenolcarbinol has the same inhibitory power as phenol, the Hg derivatives of this have a greatly increased efficiency, varying somewhat with the % of Hg; 1 compd., however, which has less Hg but in which both a NO<sub>2</sub> and a Hg group occupy the ortho position with respect to the hydroxyl group, has a higher inhibitory power. In the aniline compds. also the substitution of a Hg group greatly increases the efficiency. The NO<sub>2</sub> group also increases the inhibitory efficiency but not in the same order of position as in the nitrophenols, since the quinonoid change does not readily take place in the aniline nucleus. However, the aniline compds. having the NO<sub>2</sub> group in the ortho position and the Hg salt in the para position seem more efficient than if the order is reversed. Me and Et groups do not materially affect the antiseptic power of the aniline compds., although these compds. having Me or Et groups + NO<sub>2</sub> groups + Hg groups have a very high antiseptic power, not apparently varying much either with the % of Hg or with the relative position of the different groups. JULIAN H. LEWIS

Conductivity of bacterial cells. R. J. GREEN AND W. P. LARSON. *J. Infectious Diseases* 30, 550-8(1922).—Dead bacterial cells offer resistance to an elec. current almost if not quite equal in amt. to that exhibited by live bacterial cells. Bacterial cells growing in ordinary mediums store up diffusible salts within their bodies to a greater concn. than is found in their habitat. On death of bacterial cells from heat or HCHO there is an exchange of salts between the cells and the surrounding medium. The drop in resistance on cell death could be shown to be due in the greatest part to an exosmosis of salts into the surrounding soln. On death there is a definite decrease in the size of the cell. It appears that cond. measurements do not measure a change in permeability of bacterial membranes, but that permeability is only indicated by the exosmosis of salts from the cells killed by heat and HCHO. JULIAN H. LEWIS

Dried yeasts. H. V. EULER AND KARL MYRHÄCK. *Z. physiol. Chem.* 117, 28-40 (1921).—Doubling the quantity of yeast more than doubled the CO<sub>2</sub> production. In the case of top yeast, extn. with water had little effect on the activity of the yeast. After extn. with alc. the diminution in activity was more pronounced. With bottom yeast extn. with 2% phosphate soln. diminished the CO<sub>2</sub> production greatly. The max. activity of 1 g. dried yeast which could be attained by adding an ext. of the same yeast (with 2% phosphate) was reached when the ext. of 8 g. of yeast was employed. R. L. STEHLÉ

Lactase content and fermentative power of lactose-fermenting yeasts. R. WILL-STÄTTER AND G. OPPENHEIMER. *Z. physiol. Chem.* 118, 168-88(1922).—Preliminary hydrolysis is not necessary for the fermentation of lactose. Mixts. of dextrose and

galactose ferment more slowly than lactose. Moreover monosaccharides could never be detected in fermenting lactose solns. as they may be in fermenting sucrose solns.

R. L. STEHLER

**Peptase, lipase and invertase of hemolytic streptococcus.** F. A. STEVENS AND RANDOLPH WEST. *J. Exptl. Med.* 35, 823-46(1922); cf. *C. A.* 15, 3646.—A method is outlined by which the enzymes of hemolytic streptococcus can be extd. with comparative ease. The peptolytic enzyme is active between  $pH$  4.4 and 8.7 with an optimum action at  $pH$  7.2. It is destroyed in neutral phosphate soln. at a temp. of  $57^{\circ}$  continued for 10 min. and at  $pH$  5.0 deteriorates slowly at  $37^{\circ}$ . Conc'n. expts. with solns. of the enzyme have shown that it resembles other enzymes. It is exceedingly susceptible to  $CHCl_3$  and its action is inhibited by dilns. of gentian violet. Casein is attacked but serum albumin is not digested after 3 days at  $37^{\circ}$ . The invertase is active between approx.  $pH$  5.0 and 8.0 with an optimum at  $pH$  7.0. It is destroyed by a temp. of  $52^{\circ}$  continued for 10 min. at  $pH$  7.0 or after 6 hrs. at  $37^{\circ}$  at  $pH$  5.0. At this acidity it is more susceptible to heat than the peptase. The lipase is active above  $pH$  5.6. The greatest activity was observed at  $pH$  7.9. It is completely destroyed after heating over  $55^{\circ}$  for 10 min. and resembles the invertase in its susceptibility to acid. C. J. WEST

ABBOTT, ALEX. CREVER: **Principles of Bacteriology.** 10th Ed. revized. Philadelphia: Lea and Febiger. 686 pp. \$4.

THOMAS, P.: **Recherches biochimiques sur les protéiques de la levure.** Paris: G. Ficker. 116 pp. Fr. 15.

#### D—BOTANY

B. M. DUGGAR

**The occurrence of chitin and its significance as a systematic phylogenetic index in the vegetable kingdom.** FRITZ VON WETTSTEN. *Sitzb. Akad. Wiss., Wien, Abt. I* 130, No. 1, 3-20(1921).—From previous data it would be inferred that chitin (A) occurs in the cell membrane only of non-autotrophic thallophytes, that there exists a relation between heterotrophic nutrition and A formation, and that a similar relation exists in the animal kingdom. An extensive investigation is reported of heterotrophic forms of the following groups: (1) Flagellata, (2) Myxophyta, (3) Schizophyta, (4) Zygomycota, (5) Phaeophyta, (6) Rhodophyta, (7) Buthallophyta and (8) Cormophyta, as well as organs from plants which, otherwise autotrophic, show in their nutrition a heterotrophic nature (e. g., the gametophyte of the gymnosperms and angiosperms). Only in (7) could A be detected. Colorless forms of (1) in great numbers, (4), (5), (6) and (8), *Neottia*, *Epipogon*, *Cerallorhiza*, *Monotropa*, *Orobancha*, *Lathraea*, *Cytinus*, prothallia of many gymnosperms and embryo sacks of angiosperms were investigated. Neither in heterotrophic nor in any stage of development of autotrophic plants could A be detected. (2) and (3) could not be analyzed chemically for A, but no trace was found by microscopic methods. The stem of (2) contains keratin, a small amt. of cellulose (B) and no A, in contrast to other stems, which have no albuminous comps. in the membrane. A could not be detected in (3), but B was present in many cases and pectin was a constituent of the membrane in most cases. In (7) B made up the greater part of the membrane in most cases, though in some, like *Chlamydomonadidae*, none was detected. Only in *Geosiphon* of this group could A be found. A is characteristic of (7) alone in the vegetable kingdom, whereas B appears to be the chief constituent of nearly all groups. The complete absence of A and the rare occurrence of B distinguish sharply (3) from (7). By comparing the new data with those already published (an extensive bibliography is appended) these 8 groups are correlated with other forms of plant life in an attempt to show, by means of their A and B content, the probable phylogeny of the various groups. The chemistry of the membranes of the

thallophytes is considered very important and this study of A is preliminary to further work.  
C. C. DAVIS

**The electrolytic conductivity of dilute solutions under the influence of submersed growths.** I. FRANZ RUTNER. *Sitzb. Akad. Wiss., Wien, Abt. I* 130, 71-108(1922).—The elec. cond. of dil. solns. offers a means of detg. quant. changes in concn. of natural and artificial nutrient media and of detecting the absorption or evolution of electrolytes by cultivated organisms in this soln. This method is applied to the detn. of the  $\text{CO}_2$  content of submersed organisms and to show that it is possible to observe the assimilation of bicarbonates and to det. accurately the amt. of assimilated  $\text{CO}_2$  from known  $\text{Ca}(\text{HCO}_3)_2$  solns. In natural and artificial  $\text{Ca}(\text{HCO}_3)_2$  solns. there occurs in the presence of *Elodea* and similar  $\text{H}_2\text{O}$  plants a very rapid decrease in the elec. cond. in the light. This is shown by the loss in  $\text{CO}_2$  and pptn. of  $\text{CaCO}_3$ . When this ends, the reverse phenomenon occurs, the cond. increases considerably in the light, again to diminish in darkness. This increase in cond. in light is related to the  $\text{CaCO}_3$  present and to the previously known appearance of an alk. reaction in lighted aq. plant cultures. These phenomena do not occur in distd.  $\text{H}_2\text{O}$  or in dil. neutral salt solns. This does not agree with Hassack who states that alkali carbonates are evolved from plant cells. Since the increase in cond. due to light can be nullified by introduction of  $\text{CO}_2$ , it is concluded that extn. of  $\text{CO}_2$  takes place, due to assimilation. Yet the increase in cond. with transformation of bicarbonates into carbonates does not suffice to explain all phenomena. It must be assumed that a part of the dissolved carbonates are converted to hydroxides. This hydroxyl formation is explained on the grounds that the Ca ions are assimilated more slowly than the  $\text{CO}_3$  ions and that accordingly an ionic exchange occurs whereby in place of the excess assimilated  $\text{CO}_3$  ions, OH ions are formed in soln. Carbonates in general are assimilated, proof of which is the gradual decrease in cond. of  $\text{CaCO}_3$  and  $\text{KHCO}_3$  solns. in the light almost to the disappearance of the salts. In the dark assimilation of  $\text{KHCO}_3$  takes place extremely slowly. *Elodea* has the power of converting  $\text{Ca}(\text{HCO}_3)_2$  to  $\text{CaCO}_3$ . Numerous expts. with  $\text{Ca}(\text{HCO}_3)_2$  solns. showed a decreased cond. down to  $0.3 \times 10^{-4}$ . Since this decrease cannot be obtained by boiling a  $\text{Ca}(\text{HCO}_3)_2$  soln. and since it occurs with great rapidity in the presence of the plant, the assumption of Nathanson ("Über die Bedingungen der Kohlensäureassimilation in natürlichen Wässern, insbesondere im Meere." *Ber. math.-phys. Klasse königl. Sächs. Ges. Wiss. Leipzig* 59 (1907); *Stoffwechsel der Pflanzen Leipzig* 1910) that  $\text{H}_2\text{O}$  plants do not effect decompn. of carbonates is not justified. Though the free  $\text{CO}_2$  in aqts. detd. by its equiv. in bicarbonate is the chief nutrient assimilated, the demonstrated increase in OH ions and the preferential assimilation of  $\text{CO}_3$  ions in the form of neutral carbonates accelerate the decompn. of the bicarbonates and promote assimilation. Complete exptl. data are given.  
C. C. DAVIS

**Biological significance of plant alkaloids.** GIACOMO CIAMICIAN. *Boll. sci. tecnico* 3, No. 5; *Giorn. chim. ind. applicata* 3, 515(1921).—These substances are not waste products, but are formed from waste products of the plant chemism to serve as protection against oxidizing actions.  
ROBERT S. POSMONTIER

**Effect of cocaine on the growth of *Lupinus albus*.** A contribution to the pharmacology of animal and plant protoplasm. D. I. MACHT AND M. B. LIVINGSTON. *J. Gen. Physiol.* 4, 573-84(1922).—Cocaine, ecgonine-HCl, benzoylecgonine, MeOH, Na and Me benzoate and several mixts. of these were studied as to their effects on the growth of young roots of the lupine. The results were compared with similar expts. of animal tissues. Cocaine was the most toxic to animal tissue, but much less so to growing roots. Ecgonine-HCl was more toxic to the roots, benzoylecgonine decidedly less toxic to the roots and animal tissue. MeOH was relatively of slight toxicity to roots or animal tissue. While Na benzoate was almost non-toxic to animal tissue, it

was the most toxic compd. used for lupine roots, the toxic concn. being only 0.007%. Me benzoate ranked 2nd in toxicity for lupine roots. The effects of these drugs were not due to changes in H-ion concn. of the culture medium. The differences noted between animal and plant tissues were not explained. CHAS. H. RICHARDSON

FRANZEN, HARTWIG: *Über die chemischen Bestandteile grüner Pflanzen*. Heidelberg: Carl Winter.

GRAFE, VIKTOR: *Chemie der Pflanzenzelle*. Berlin: Gebr. Borntraeger. 421 pp. M 105.

MOLISCH, HANS: *Mikrochemie der Pflanze*. 2nd Revised ed. Jena: Gustav Fischer. 434 pp. M 58. Reviewed in *Naturwissenschaften* 10, 209(1922).

### E—NUTRITION

PHILIP B. HAWK

#### NORMAL

**Influence of temperature on the utilization of the reserves during inanition.** F. TERROINE AND H. BARTHELEMY. *Arch. intern. physiol.* 19, 88-102(1922).—When homeothermic animals are subjected to different temps. during inanition prolonged to exitus it is observed that the higher temp. occasions the greater loss of wt. All the animals had the same fat and lipid content at the end of the expts. whatever the temp. to which they had been subjected. These facts justify the conception of a quant. sepm. of fatty acids into 2 groups. One, the variable element, made up of the fat reserves of the body which are used up during starvation, the other, the const. element, the integral lipoids of the cells, characteristic of the species. F. S. HAMMETT

**The influence of the addition of adsorbents to a one-sided diet in the production of avitaminosis.** N. MESSERLI. *Arch. intern. physiol.* 19, 103-14(1922).—Rats and pigeons were fed decorticated rice with and without the addition of blood-charcoal or *Bolus alba*. The adsorbents apparently accelerated and aggravated the onset of the characteristic symptoms of avitaminosis and did this in proportion to their adsorptive power. F. S. HAMMETT

**Artificial feeding of pigeons and its relation to avian polyneuritis.** J. HOET. *Arch. intern. physiol.* 19, 115-28(1922).—H. gave a diet of 18 parts of casein; 11 of butter; 4 of sugar; 54 of starch; 5 of margarine; 4 of filter paper and 4 of salt mixt. mixed with 20% H<sub>2</sub>O to a stiff paste. This was baked at 110°. The ration is deficient in vitamin B. Its substitution for the usual diet of polished rice or sterilized grains produces several advantages which are discussed. F. S. HAMMETT

**Metabolism during vitamin-free feeding.** M. TSUJI. *Biochem. Z.* 129, 194-207 (1922).—A 11-kg. dog was fed 50 g. dried horse-meat, 29 g. butter, 50 g. rice, 3 g. NaCl and 750 cc. H<sub>2</sub>O daily for 3 weeks. The diet was then changed to 44 g. wheat protein, 20 g. lard (purified), 60 g. rice, 3 g. NaCl and 750 cc. H<sub>2</sub>O for 107 days. The N content of the 2 diets was the same. The fact that the animal remained in N equil. for almost 52 days of the vitamin-free period showed that the N of the wheat protein replaced the N of the meat of the fore-period. Analyses of urine and feces showed that intestinal absorption was good throughout the expt. and hence not interfered with by lack of vitamins. The loss of wt. can, therefore, not be attributed to incomplete absorption. The fore-period showed slight N retention of from 0.3 to 0.4 g. per day. During the vitamin-free diet this gradually fell till it became slightly negative on the 52nd day and markedly negative by the 69th. The loss of N decreased gradually in amt. until by the 97th day when retention was again observed; this lasted until the 107th day when the dog died. T. favors the idea of inhibition of N excretion as the explanation of the terminal retention, rather than protein storage. F. S. HAMMETT

**The biological evaluation of the foodstuffs.** L. BERCZELLER. *Biochem. Z.* 129,

217-58(1922).—This series of studies is divided into 7 sep. papers, the general results of which are given in the last. The titles and pagination are as follows: **The role of the specific nature of the proteins in nutrition.** Leguminosae. *Ibid* 239-50. **The role of taste in nutrition.** *Ibid* 251-69. **Grains used in bread.** *Ibid* 270-88. **Studies of milling processes.** *Ibid* 289-312. **Studies of soy-bean meal.** *Ibid* 313-19. **The biological correlation between mainly protein and mainly carbohydrate diets.** *Ibid* 320-58.—Rats and mice were used in the expts. When rats are fed starches (carbohydrates) they live longer than when they are starved at either room or body temp. or when fed on an exclusively protein diet. The addition of 5 to 20% of fat to the starch diet prolongs the lives of the animals. Too much fat (50%), on the other hand, shortens their lives. When a paraffin-oil starch mixt. is fed the animals live a much shorter period than when actual fat is given. 50% of oil shortens life almost the same as does starvation (active harmful effect of paraffin oil). Butter acts quite differently from the other fats. Legumes which are closely allied both in systematic order and chem. properties have quite different values in their ability to maintain life. Both rats and mice live longest on lentils, less long on peas and shortest on beans. The cost of these legumes runs parallel with their maintenance values (the ability to maintain life). A one-sided leguminous diet produces characteristic pathological symptoms, males usually failing to survive as long as the females. When peas and beans are heated their maintenance value is increased; when lentils are similarly treated it is decreased. The active leguminous effect is related to the character of the proteins, and the heat effect is the greater, the greater the protein effect (on maintenance) though the effect of heating cannot be reduced to a single cause. The studies on the choosing of food by the rats in general indicated that to a certain degree that choice was exerted which was most suitable in relation to the length of life and was typical for individual rats. Apparently it is a matter of indifference whether the whole seeds are fed as such or given as heat-inactivated meals. In fact the animals will not take one food material alone that will alone prolong their lives when 3 are offered. When beans are fed with corn to young animals the length of life is much shortened even if small amts. are ingested. When rats were offered barley, rye and wheat they ate each grain almost exclusively in succeeding periods in the order given. The duration of the barley and rye periods was almost the same for the individual animals. Characteristic sex differences were also observed. The males ate less rye than the females. Similar results were obtained with corn. The process of milling markedly changed the biological values of the cereals. Wheat is lowered in value, as is soy bean. B. believes that the biol. value of protein-contg. foods depends in part on the physical characteristics (such as imbibition). Wheat is of value to rats because of its H<sub>2</sub>O-sol. extractives. When milk powder is fed with other foods the rats eat it greedily, so that the choice of foodstuffs follows a law of mass action. In fact these studies show a simple mass law relation between length of life and food intake. Small alterations in single foodstuffs markedly influence the amt. of total food intake.

F. S. HAMMETT

**Deficient diets and hormone activity. I. Studies of the effect of the simultaneous influence of deficient diet and thyroid feeding on the growth and development of frog larvae.** F. GROSBEELS. *Z. Biol.* 75, 91-120(1922).—An increase in the protein content of the H<sub>2</sub>O ext. of the thyroid causes an increase in the growth retardation and developmental acceleration of frog larvae. AcOH has no influence on growth or development. Dog-muscle bouillon and "biotose" may retard both growth and development, the one is attributed to a protein-sparing action of fat, the other to a similar effect of sugar. When the larvae are fed vitamin-poor piscidin alone, the growth is accelerated over that present with normal H<sub>2</sub>O ext. of the thyroid; while feeding with vitamin-poor thyroid ext. plus piscidin markedly retards growth as compared with the controls.

When the larvae are first fed on a vitamin-poor diet and then overfed, growth may be markedly increased even if thyroid ext. is simultaneously given, but the developmental effect of the latter is not influenced.

F. S. HAMMETT

**Basal metabolism. Critical study of a simplified method.** DAUTREBANDE AND WHITRIDGE DAVIES. *Bull. acad. roy. m.d. Belg.* [5] 2, 147-70(1922).—After a general discussion a simplified procedure is described in great detail, based on the use of a Douglas bag and a modified Haldane mask, a sketch of which is given. Causes of error are discussed, as well as the precautions necessary for their avoidance. Protocols of clinical cases are given.

M. HEIDELBERGER

**Effect of diet on the weight of the hypophysis and thyroid gland of the albino rat, and on the action of their extracts on the isolated small intestine.** L. M. DEGENER. *Am. J. Physiol.* 59, 107-18(1922).—Five diets were used viz. (1) oatmeal and milk, (2) vegetables, (3) meat, (4) standard + KI, (5) standard + thyroxin. On the oatmeal, vegetable and meat diets the thyroids were slightly larger than in the controls. On the oatmeal diet the hypophyses were slightly larger than, on the vegetable diet smaller than, while on a meat diet no different than, in the controls. KI and thyroxin seemed to have no effect on the size of the glands. Exts. of hypophyses from the oatmeal and vegetable diet caused contraction of isolated intestinal strips; the control ext. always caused relaxation. This may be due to the relative proportion of glandular and nervous portions of the glands; the glandular lobe ext. caused contraction, the nervous lobe caused relaxation. There was no difference in the action of thyroid exts. from the different diets.

J. F. LYMAN

**Weight regulation in the adult human body during over-nutrition.** A. GULICK. *Am. J. Physiol.* 60, 371-95(1922).—During periods aggregating about 370 days on an exptl. diet, a man of the difficultly fattening type was found to owe his resistance against fattening to an extravagant calorie requirement which persisted at all times, despite a moderate daily round of activities. This extravagance increased during a period of excessive carbohydrate diet, during which there was about 20% increase in wt., and stayed above the initial level even after the return to normal wt. The basal metabolic rate was not involved, but remained strictly normal. The high calorie output and consequent resistance against fattening may find its explanation either in a condition of N enrichment, or in an upward variation of the "cost of digestion" (and assimilation) of starchy food.

J. F. LYMAN

**The relations between fertility and nutrition. I. The ovulation rhythm in the rat on a standard nutritional regime.** H. M. EVANS AND KATHERINE S. BISHOP. *J. Metabolic Res.* 1, 319-33(1922).—Preliminary study of ovulatory rhythm of rats when fed adequate rations. A generous mixed table scrap ration and a standard McCollum ration were fed to a large number of rats. No differences were observed in the behavior of the rats in the two groups. It was established that in 80% of the normally fed rats the first estrus occurred between the 37th and 55th day, av. on the 47th day, and that 75% of the estrus cycles are 5 days or less in length, the rest are of longer duration.

**II. The ovulation rhythm in the rat on inadequate nutritional regimes.** *Ibid* 335-55.—The limitation of intake (under-nutrition) of standard McCollum diet delayed sexual maturity and suppressed estrus changes in rats to an extent depending upon the degree of starvation to which the animals were subjected. These suppressions were not correlated exactly with body wt. changes or with variations in rate of growth, but in general the greater stunting resulted in the more marked disturbances of ovulation. On carbohydrate-free diets with protein supply being ample but not high, no marked change in either growth or ovulation rhythm occurred. With carbohydrate-free rations low in protein (12% casein) the rats did not consume enough protein because of unpalatability of diet; stunting, delayed maturity and fewer estrus periods resulted.

Carbohydrate-free diets high in protein, 91% casein, delayed growth and maturity and reduced greatly the number of estrus cycles. This effect is ascribed to excess of protein and not to lack of carbohydrate, the withdrawal of which does not appear in these studies to be deleterious to the rat. Fat-free diets with varying proportions of protein and carbohydrate produced marked disturbances in ovulation even when growth was normal. With the substitution of casein by wheat, a qualitatively deficient protein, in the standard diet of young rats, their sexual physiology and development were profoundly disturbed along with stunted growth. Normal conditions were restored by adding casein to the diet. The removal of the salts from the standard diets caused considerable sex impairment in excess of the growth impairment. Withdrawal of fat-sol. vitamin A from the diet to an extent insufficient to cause growth failure or xerophthalmia produced a highly characteristic disturbance of estrus. The disturbance consisted in the prolongation of the estrus desquamative change in the vaginal epithelium, which occurred throughout the period of acute deficiency. The rats continued to ovulate and to form corpora lutea irregularly in distinction from rats fed on diets insufficient in water-sol. B, in which case ovulation ceased completely until vitamin B was restored in the diet. When the rats were fed on meat alone or milk alone no great growth delay was observed while maturing was delayed and the number of estrus cycles greatly depressed. The above changes in the sexual physiology of the rats constitutes a more delicate test for nutritional deficiencies than the usual one of growth rate. W. A. PERLZWEIG

**The important results of researches in nutrition metabolism and growth in 1914-1919.** HANS ARON. *Monatsschr. Kinderheilk.* 17, 257-90(1921).—A good review and an extensive bibliography. W. A. PERLZWEIG

**Modern nutrition problems.** A. DURIG. *Wiener klin. Wochschr.* 34, 83(1921).—Reflections on post-war nutritional problems in Central Europe, with special emphasis on the feasibility of low-protein nutrition and on the need of reduction and reclamation of various food wastes. W. A. PERLZWEIG

**Organic foodstuffs with specific action. II.** E. ABDERHALDEN. *Arch. ges. Physiol.* (Pflüger's) 182, 133-56(1920); cf. *C. A.* 16, 736.—Detailed protocols are presented showing the therapeutic effect of the addition of yeast or yeast exts.—alc., acetone, and alc.-acetone— to diets of polished rice fed to pigeons. Even small ants. of the yeast protected against alimentary dystrophy. The benefits of the yeast quickly disappeared when this substance was eliminated from the diet. G. H. S.

**Organic foodstuffs with specific action. III.** E. ABDERHALDEN AND L. SCHMIDT. *Arch. ges. Physiol.* (Pflüger's) 185, 141-6(1920); *Physiol. Abstracts* 6, 140.—Inconclusive expts. on O consumption of muscle from normal and beriberi pigeons and on the effects of yeast and muscle ext. on the respiration of such (as of other) muscle. H. G.

**Organic foodstuffs with specific action. VII.** EMIL ABDERHALDEN AND ERNST WERTHEIMER. *Arch. ges. Physiol.* (Pflüger's) 191, 258-77(1921).—The effect of a large series of very varied substances upon gaseous metabolism was detd. The substances which caused an increase were quite diverse in nature, e. g., glutamine, glutaminic acid, pyrrolidinedicarboxylic acid, cod-liver oil and rape oil, tryptophan, arsenites, hexose phosphate, and such acids as formic, tartaric, citric, hydroxybutyric, hydroxyisocaproic, pyruvic, lactic, and valeric. Antiscorbutic substances also caused an increase. Respiration in plants was caused by yeast ext. The respiration of human erythrocytes was not affected by light, although if the cells were "sensitized" by eosin changes were noted, some intensities causing an inhibition, others causing an acceleration in the respiration. VIII. EMIL ABDERHALDEN. *Ibid* 278-301.—A reduced gaseous exchange resulted when guinea pigs were fed on a scorbutic diet. The addition of yeast to the diet increased the exchange. G. H. S.

**Protein minimum. VI. Formation of mercapturic acid on a low nitrogen diet.** J. KAPRAUMER. *Z. physiol. Chem.* **116**, 302-7(1921).—On an almost N-free diet when PhBr was fed and cystine administered subcutaneously mercapturic acid was excreted. In the control period when PhBr was administered but no cystine no mercapturic acid was excreted.

**The physiological value of the vitamins.** A. D. EMMETT. *J. Am. Pharm. Assoc.* **10**, 176-82(1921).—Essay and discussion.

R. L. STREHL  
L. E. WARREN

#### ABNORMAL

**Basal metabolism and food consumption of underweight college women.** KATHERINE BLUNT and VIRGINIA BAUER. *J. Home Econ.* **14**, 171-80, 226-32(1922); cf. *C. A.* **16**, 738.—The basal metabolism of 19 nervous, underweight college women was almost normal, while the food consumption was low, 37.3 cal. per kg. L. D. E.

**Basal metabolism of women and underweight children.** KATHERINE BLUNT. *J. Home Econ.* **14**, 117-20(1922); cf. *C. A.* **16**, 1263.—Recent investigations in the author's lab. are briefly discussed.

HELEN N. ELLIOTT

**Basal metabolism study in a case of congenital myxedema treated with thyroid extract.** NOBÉCOURT and H. JANET. *Bull. mun. soc. m'd. hosp. Paris* **38**, 608-11(1922).—Basal metabolism was increased under treatment with thyroid ext. F. S. HAMMETT

**Experimental rickets in rats.** V. KORENCHESKII. *N. Y. Med. J.* **115**, 612-4(1922); cf. *C. A.* **16**, 278.—The expts. of K. show that the vitamin A deficiency alone is capable of causing rickets in rats. They also indicate the importance of Ca deficiency especially when combined with vitamin deficiency. It is believed that only special forms of Ca salts are effective in relieving rickets. The method of administration is also important. The same may be true for vitamin A.

F. S. HAMMETT

**The basal metabolic rate in constitutionally inferior children.** H. O. POLLOCK and E. B. MCCREADY. *Penn. Med. J.* **25**, 556-7(1922).—Brief descriptions of cases which yield the conclusion that the basal metabolic rate affords a means of classification of the cases and serves as a guide to therapy.

F. S. HAMMETT

**Experiments on carbohydrate metabolism and diabetes. IV. Dextrose-nitrogen ratios in partially depancreatized dogs.** F. M. ALLEN and MARY B. WISHART. *J. Metabolic Res.* **1**, 97-107(1922); cf. *C. A.* **15**, 890, 2908.—The following conclusions and suggestions are made particularly with reference to the question of a plurality of internal secretions of the pancreas and the sep. functions of the beta cells and of the elements remaining after the degeneration of the beta cells. Total pancreatectomy does not invariably give rise to a permanent "total" dextrose (D):N ratio of 2.8:1. A totally depancreatized animal with a lower ratio may be as completely diabetic as one with the maximal D:N ratio, and it is improbable that the missing glucose or glucogenic material is normally utilized. Incompletely depancreatized animals sometimes show a total D:N ratio of 2.8:1 and sometimes lower ratios. The D:N ratio is, therefore, not an infallible test for deciding whether the entire pancreas has been removed. Diabetes of fatal severity may exist when the D:N ratio is rather low. In some of these cases glucosuria may be stopped by fasting, in others it may not. If any animal shows the maximal ratio treatment is hopeless and the outcome is always fatal. This difference from the experience with human cases is explained by the fact that in exptl. animals the diabetes rests solely upon an organic deficiency and not upon a functional disorder. Animals which have lost all beta cells may show submaximal D:N ratios, while in partially depancreatized animals showing "total" D:N ratios the complete vacuolation or degeneration of the beta cells is invariably found. The metabolic differences between partially (A) and totally (B) depancreatized dogs are classified as follows: (1) The loss of both sugar and nitrogen by B is higher than that by A. (2) The total basal metabolism is probably higher in B than in A in consequence of greater protein break-



down and because of general melting down of tissues from lack of pancreatic secretion. (3) Better spirits, muscular strength, less severe cachexia and prostration, far longer life of A as compared with B. B does not die from tissue starvation nor from mere loss of sugar. The power of wound healing and of resistance to infection is practically abolished in B as compared with A.

W. A. PERLZWEIG

**Alcohol in the diabetic diet.** F. M. ALLEN AND MARY B. WISHART. *J. Metabolic Res.* 1, 281-306(1922).—Expts. were made with 2 diabetic patients with addn. of varying amts. of EtOH to diets contg. varying quantities of protein, fat and carbohydrate on fasting days. Alc. is not converted into sugar or acetone in the body; it exerts no antiketogenic effect; "luxus" diets formed with addition of alc. or of alcohol and fat to a standard diet give rise to less acidosis than similarly excessive diets built up by addition of fat alone; when under-nutrition diets are converted into "luxus" diets by addition of alc. an increase in acetone production may result; alc. cannot be used in the treatment of coma; addn. of alcohol failed to increase wt. and strength of patients as it failed in the case of added fat. The expts. with alc. are claimed to furnish important support to the under-nutrition treatment of diabetes, on the general basis of the harmful results of overloading the total metabolism. (Cf. *Rockefeller Inst. Monogr.* No. 11 (1919).)

W. A. PERLZWEIG

**Overnutrition with fat and alcohol in severe diabetes.** F. S. LECHE. *J. Metabolic Res.* 1, 307-17(1922).—100-120 g. EtOH or 137-158 g. fat added daily to the diets contg. 1000-1100 calcs. of two severe diabetics produced marked hyperglucemia, slight glucosuria and ketonuria. The results of Allen (cf. preceding abstr.) and of Mosenthal and Harrop (*C. A.* 13, 467) are confirmed.

W. A. PERLZWEIG

WORINGER, PIERRE: *La dégradation des acides gras dans l'organisme animal.* Paris: Masson et Cie. 140 pp. Fr. 8.

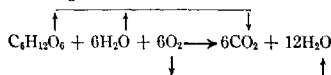
## F—PHYSIOLOGY

ANDREW HUNTER

**Physiological chemistry.** LUDWIG PINCUSSEN. *Fortschritte Chem.* 17, 33-62 (1921).—Important progress in 1915-19.

C. C. DAVIS

**Is there a genetic relation between the oxygen inhaled and the oxygen of the exhaled carbon dioxide?** TORSTEN THUNBERG. *Naturwissenschaften* 10, 417-20 (1922).—A theory is developed depending upon the conception that H is the basic, elementary combustible of the living cells. This H is activated by catalyzers, and in this active form can be oxidized directly by O at a low temp. The decompn. of the complex compds. occurs through a series of progressive dehydrogenations effected by a series of enzymes, each of which has a definite and limited sphere of activity. The H split off by the enzymes is oxidized directly to H<sub>2</sub>O. This decompn. by oxidation is accompanied by a second phenomenon, an addn. of H<sub>2</sub>O and splitting off of CO<sub>2</sub>. The dehydrogenation means a loss of 2 H atoms; this leaves a product richer in C and O and poorer in H than the original. By an accompanying loss of CO<sub>2</sub> the mol. is thus progressively diminished. In short it is contended that inhaled O is utilized to form H<sub>2</sub>O with H activated by sp. enzymes, and furthermore that there is no relation between inhaled O and exhaled CO<sub>2</sub>. The latter is formed only by splitting off successively from the progressive decompn. products of the original complex compd. CO<sub>2</sub> also arises indirectly from the H<sub>2</sub>O mols. which are added to the complex compd. at the double bond formed by removal of H. In this way the usual equation  $C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O$  must be changed to



to conform with this reasoning. This conception can be supported by theories of combustion reactions presented by Dixon (*J. Chem. Soc.* 49, 94(1886)) and by Wartenberg (*C. A.* 15, 814).

C. C. DAVIS

**Results obtained at the physical test station, Edinburgh.** HENRY BRIGGS. *Proc. Roy. Soc. Edinburgh* 42, 34-42(1922); cf. *C. A.* 15, 2484.—*Fitness* is defined as the efficiency of oxygenation of brain, heart and muscles during exercise. Details of the construction and operation of a device used to measure fitness are described. Of all men over 40 years of age who were examd., only 20% were evidently worth training for military service. Results of some individual exams. are given.

D. B. DILL

**Comparative examination of sedimentation rate of blood corpuscles in citrated blood and stalagmometric quotients.** W. SCHEMENSKY. *Münch. med. Wochschr.* 67, 1228-9(1920); *Physiol. Abstracts* 6, 186.—When blood is left to stand *in vitro*, the rate of sedimentation of red cells is observed. This rate is increased in blood from cases of pregnancy and various pathological conditions. S. finds, in 70% of hospital cases examd., an increased rate of sedimentation of red cells goes hand in hand with a lowered surface tension in the urine. (Cf. *C. A.* 15, 386.)

H. G.

**The action of heterogeneous proteins in the organism.** A. LÜTTICHAU. *Arch. intern. physiol.* 19, 1-16(1922).—L. injected solns. or suspensions of egg albumin, egg globulin, human saliva, casein, horse serum, gelatin, ascitic fluid and Witte peptone intravenously into dogs and studied the effect on the blood sugar. Hyperglucemia but not glucosuria was produced by the ova-proteins, salivary proteins, and casein. The hyperglucemia produced by egg white is due to its globulin content. No question of direct enzyme activity is allowable since none of the substances save saliva had any diastatic action on glycogen *in vitro*. The phenomenon is considered as probably a glucose mobilization.

P. S. HAMMETT

**The glycogen of the specific mechanism of the heart in its relations to cardiac function.** I. S. LAFRANCA. *Arch. intern. physiol.* 17, 266-70(1922).—Glycogen is found in the peripheral part of the cells of the sino-auricular node in the form of granules or falciform masses. When tachycardia is induced by caffeine there occurs a marked reduction in the glycogen content of these cells.

F. S. HAMMETT

**The hemochrome of Herzfeld and Klinger.** S. PARTOS. *Biochem. Z.* 129, 89-100(1922).—A series of studies on the problem of the structure of hemoglobin raised by Herzfeld and Klinger (*C. A.* 14, 2348). P. believes that the so-called mother substance "hemochrome" of hematin, hemin, etc., of these workers does not exist and that the compd. they were studying was actually hematin. Hematin and "hemochrome" have identical properties. Both are produced when blood is warmed with  $\text{NaHCO}_3$ ; both are insol. in abs. alc.; both are sol. in  $\text{Na}_2\text{CO}_3$  and in pyridine. They both show absorption bands between 620 and  $580\mu$ . The acetic acid soln. of hemochrome has an absorption band at 640 to  $630\mu$ ; the HCl soln. of hematin has its band at 644 to  $633\mu$ . When the bicarbonate alc. soln. of either is treated with a little  $\text{NH}_4\text{OH}$  and a few drops of a 25% soln. of hydrazine sulfate the two bands of hemochromogen are produced. Charts are given of the spectrophotometric studies of the  $\text{NaHCO}_3\cdot\text{H}_2\text{O}$  soln. of hematin and "hemochrome."

F. S. HAMMETT

**Residual reduction.** M. LJUNGDAHL. *Biochem. Z.* 129, 111-4(1922).—A discussion of Ege's study of the problem (*C. A.* 15, 111) and expts. which show that "glucolysis" in defibrinated or oxalated blood occurs with quite as much facility without yeast as when the organism is present. This decrease in detectable reducing substances of the blood is hence independent of yeast fermentation even if such be present and hence it may not signify a disappearance of sugar.

F. S. HAMMETT

**The effect of secretin solutions on intestinal motility.** K. HARAMAKI. *Biochem. Z.* 129, 128-33(1922).—Using the Katsch (*Z. expl. Path. Ther.* 1912, 12; cf. *C. A.* 8,

162) method of observation H. found that the intravenous injection into the ear-vein of rabbits of histamine, whey-secretin, or spinach-secretin produced slight colonic peristalsis and marked duodenal activity. Decoction of roasted barley had only slight and uncertain effect. NaCl had no action. The peristalsis occurred within 2 or 3 mins. after the injections and lasted for 20 to 30 mins. This rapid onset of peristalsis is interpreted as signifying a primary action of the chem. compds. on the motor app. of the gut.

F. S. HAMMETT

**Calcium combination by animal tissues. VII.** E. FREUDENBERG AND P. GYÖRGY. *Biochem. Z.* 129, 134-7(1922); cf. *C. A.* 16, 937.—Studies on the problem of anion effect by the methods of ultrafiltration and imbibition. Serum, to which a small amt. of Ca was added, plus 2 cc. of *N*/6 solns. of KCl, KNO<sub>3</sub>, KC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>, K<sub>2</sub>HPO<sub>4</sub> or KHCO<sub>3</sub> was dild. 10 times with 0.9% NaCl and subjected to ultrafiltration. The results are in agreement with the earlier reported dialysis expts. The amt. of ultrafiltration Ca was greatest with KCl. The imbibition expts. were carried on with cartilage and showed that when this tissue has been suspended in CaCl<sub>2</sub> it loses its swelling capacity the least as compared with the control. Creatinine does not have the slightest effect on the imbibition. Creatine facilitates swelling. The studies are taken to indicate that the influence of anions on Ca combination by tissue colloids is not attributable to the hydron effect. **VIII.** *Ibid* 138-43.—Further studies with org. compds. showed that HCHO and glucose inhibit Ca combination by cartilage, while BtOH and acetone do not influence the process when present in 0.1 *N* concn. The reaction velocity increases with rising temp. This is taken as a proof of the chem. nature of the combination of Ca with tissues.

F. S. HAMMETT

**The significance of the potassium and calcium ions for induced edema and the diameter of the blood vessels.** R. J. HAMBURGER. *Biochem. Z.* 129, 153-62(1922).—An attempt to find a perfusion liquid with which the vascular system of the frog can be irrigated without producing edema in the hind legs of the animal. K or other radioactive elements such as U, Th or Rb can be omitted from the perfusion fluid without edema only when the liquid contains a sharply defined amt. of Ca<sup>++</sup> equiv. to CaCl<sub>2</sub>·6H<sub>2</sub>O 0.007%; edema appears if 0.006% Ca is used, or if 0.01% KCl is added. This result is interpreted as meaning that the contracting effect of Ca is set aside by the antagonistic K ion. The finding of Gunzberg (*C. A.* 12, 2617) that Ringer soln. with 0.02% NaHCO<sub>3</sub> does not produce edema is explained by the fact that in this soln. an excess of Ca ions is present, a part of which is neutralized by the K. Hence the inhibition of edema is not a sp. radioactive effect of K, but an expression of the K-Ca antagonism. When the vascular system of the frog is perfused with a mixt. of 0.6% NaCl + 0.01% CaCl<sub>2</sub>·6H<sub>2</sub>O contractile occlusion occurs which prevents further irrigation. If a trace of KCl be added perfusion is renewed. This action is reversible. This parallelism of vascular contraction and vascular condensation is observed also under the influence of O<sub>2</sub>.

F. S. HAMMETT

**Comparative studies of the activity of the secretin of the digestive tract.** K. HARAMAKI. *Biochem. Z.* 129, 503-6(1922).—The mucosa of fundus, duodenum, small intestine, large intestine and rectum produces a "secretion" stimulating secretion of the gastric cells. Subcutaneous exts. of the above tissues acted about alike, save that the jejunal ext. gives slightly less stimulation. When the exts. were given by mouth a slight effect was observed.

F. S. HAMMETT

**The distribution of sugar between corpuscles and plasma.** W. FALTA AND M. RICHTER-QUITTNER. *Biochem. Z.* 129, 576-81(1922).—Polemical in reply to the criticisms of Brinkman and Van Dam (*C. A.* 14, 3104) and Van Crevell and Brinkman (*C. A.* 15, 3642) and others.

F. S. HAMMETT

**Studies of the thyroid apparatus. V.** The significance of the comparative mor-

**ality rates of parathyroidectomized wild Norway rats and excitable and non-excitable albino rats.** F. S. HAMMETT. *Endocrinology* 6, 221-9(1922); cf. *C. A.* 15, 4023.—The mortality of wild Norway rats is 90% after parathyroidectomy as compared with a rate of 78% for excitable albino rats and 13% for gentle animals. All results are on a basis of death due to parathyroid tetany within 48 hrs. The findings are considered as support for the idea that parathyroid tetany is due to the accumulation in the organism of certain toxic compds., probably methylguanidine or allied substances, which the functioning parathyroids prevent. The basis of the correlation between susceptibility to parathyroid tetany and production of toxic bases through muscle tension is discussed in some detail.

F. S. HAMMETT

**The effect of body tissues other than the thyroid upon the basal metabolic rate.** J. C. AUB AND M. TAYLOR. *Endocrinology* 6, 255-69(1922).—A review. F. S. H.

**The external function of the pancreas and its bearing on the surgery of the pancreas.** J. J. GILBRIDE. *N. Y. Med. J.* 115, 470-2(1922).—Of medical interest. F. S. H.

**A comparison of successive aspirates of the gastric contents.** B. C. LOCKWOOD AND H. J. JACOBSON. *N. Y. Med. J.* 115, 493-5(1922).—Different portions of the stomach contents aspirated in quick succession, through a small tube, show a moderate variation in phys. character and acid contents. There is obtained a picture of the cycle of events as they occur in the mechanically and chemically active portions of the stomach. Such fractional gastric analysis can give instructive results. F. S. H.

**Physiology of the blood vessels of the placenta.** W. SCHMITT. *Z. Biol.* 75, 19-78(1922).—The blood vessels of the placenta differ from the usual in the distribution of their musculature. No nerve supply could be found by histological study. Nevertheless the vessels are very sensitive to various agents. When the placenta is perfused with histamine, pituglandol or  $\text{BaCl}_2$  vasoconstriction occurs; when amyl nitrite is used vasodilatation is observed. Adrenaline produced no effect. Isolated bits of vascular tissue responded similarly. The anomalous effect of adrenaline leads to the conclusion that this compd. is almost sp. in its action on nerve endings and that its effect on smooth muscle is minor. The placenta vessels are extraordinarily sensitive to O supply.

F. S. HAMMETT

**Action currents in stomach and intestine.** W. C. ALVAREZ AND L. J. MAHONEY. *Am. J. Physiol.* 58, 476-93(1922).—New electrodes and other app. have been devised, by means of which the action currents of the digestive tract have been studied. Large currents are obtained from stomachs and bowels which, to the naked eye, show no peristaltic movement. Splanchnic stimuli which inhibit the contractions of the bowel have little or no effect on the rhythmic action currents.

J. F. LYMAN

**The role of the sodium and the carbonate ions and of the change in the sodium-calcium ratio in the contraction of the isolated duodenal segment of the albino rat.** F. S. HAMMETT AND J. E. NOWREY, JR. *Am. J. Physiol.* 59, 48-51(1922).—The contraction of the isolated duodenal segment of the albino rat which follows the addition of 0.1 M  $\text{Na}_2\text{CO}_3$  soln. to oxygenated Tyrode's soln., in which the segment is suspended, is not due to the increase in Na ions, in the Na:Ca ratio, or in the carbonate ions. Na may participate in the effect by increasing cell permeability, but it cannot be considered as the primary cause of the contraction.

J. F. LYMAN

**The role of the change in hydrogen-ion concentration in the motor activities of the small intestine.** F. S. HAMMETT. *Am. J. Physiol.* 59, 52-8(1922).—The contraction in isolated duodenal segments of the albino rat which follows the addition of  $\text{Na}_2\text{CO}_3$  soln. to oxygenated Tyrode's soln. in which the segment is suspended is due to the increase in  $\text{OH}^-$  concn. of the liquid. Changes in the  $\text{H}^+$  and  $\text{OH}^-$  concn. of the material coming in contact with the intestine are important participants in the regulation and control of intestinal motor activities. The action of  $\text{OH}^-$  on intestinal muscle is through neural mechanisms.

J. F. LYMAN

**Electrical conductivity of animal tissues under normal and pathological conditions.** C. W. CRILE, H. R. HOSMER AND A. F. ROWLAND. *Am. J. Physiol.* **59**, 59-106(1922).—App. and methods used are described. 4764 sections from 455 rabbits and 219 sections of pathol. human tissues were measured. Influences which affect the general physical condition of the organism produce changes in elec. cond. in the dominant reactive tissues; these changes are uniformly and measurably manifested in the brain and the liver. Apparently these changes in cond. appear more promptly than any gross clinical alteration. It is believed that elec. cond. measurements provide a means whereby to further the interpretation of the normal operation of the organism, and whereby to measure the progress of pathol. processes within the various organs and tissues. J. F. LYMAN

**Variations in output of bile salts and pigments during twenty-four-hour periods.** F. P. WISNER AND C. H. WHIPPLE. *Am. J. Physiol.* **59**, 119-33(1922).—With standard bile fistula dogs there is little if any difference in the output of bile, bile salts or bile pigments during 4 consecutive 6-hr. periods. Large doses of taurocholic acid cause a prompt rise in bile salt excretion so that practically all is excreted within 6 hrs. after its ingestion. The cholagogue action persists during the second 6-hr. period; while the bile-pigment output remains const. throughout. Bony abnormalities were noted as related to the const. loss of bile. J. F. LYMAN

**The relation between nervous and hormone control of the respiratory center.** J. J. R. MACLEOD AND S. U. PAGE. *Am. J. Physiol.* **59**, 134-50(1922).—Expts. with decerebrate cats show that the reflex excitability of the respiratory center is not altered by changes in the respiratory hormone (H-ion and CO<sub>2</sub> concn.) of the arterial blood. J. F. LYMAN

**Influence of blood serum on the coagulative activity of tissue extracts.** C. A. MILLS AND S. MATHEWS. *Am. J. Physiol.* **59**, 193-201(1922).—Rabbit serum is capable of causing as high as a 30-fold increase in the coagulative activity of lung ext. This effect is gradually replaced by a diminution in the activity of the ext. below the original as the mixt. is left standing. Human serum has the same power to a less degree. The high toxicity of some protein solns., such as organ exts. or blood serum, may be explained by the activation of the injected protein by the patient's blood resulting in intravascular clotting. No theory is advanced to explain the phenomenon. J. F. L.

**The relation of splenectomy to growth and appetite in the rat.** A. H. SMITH AND LEAH ASCHAM. *Am. J. Physiol.* **60**, 250-1(1922).—White rats, on which splenectomy had been performed at the age of 40 days, showed no appreciable variation from the normal in appetite, rate of growth and red blood cell count. Splenectomized rats reproduced successfully and the second generation grew normally after splenectomy. Splenectomy had no effect on the development of the organs and bones. J. F. L.

**The relation of the adrenals to fatigue.** F. A. HARTMAN, R. H. WAITE AND E. F. POWELL. *Am. J. Physiol.* **60**, 255-69(1922).—Cats with one adrenal and that denervated have a low epinephrine supply as indicated by the denervated pupil reaction. Such cats show a loss of appetite, loss of wt., change of temp. and weakness. After regeneration of some of the nerve fibers, health and power to work are regained. Frequently cats with adrenal deficiency developed convulsions when working on a treadmill. The results indicate that epinephrine plays a very important part in increasing muscular work and delaying the onset of fatigue. J. F. LYMAN

**The significance of hydremia in the secretion of urine.** H. BAKWIN. *Am. J. Physiol.* **60**, 343-9(1922).—In infants, hydremia alone does not cause diuresis. Water drinking causes a moderate hydremia without diuresis; after saline drinking there was a marked blood diln. and decreased urine elimination. J. F. LYMAN

**The secretory action of the pancreas in relation to the thyroid gland. I. The effect of thyroid feeding in rats upon the secretory action of the pancreas.** H. HASHI-

**MOTO.** *Am. J. Physiol.* **60**, 357-64(1922).—Feeding white rats rather large amts. of dried ox thyroid (0.2 to 0.3 g. per day) decreased the amylase content of the pancreas gland and the amylase found in the small intestine; feeding smaller amts. (0.1 g. per day) caused an increase in amylase in the pancreas and intestine. **II. The effect of thyroidectomy in rats upon the secretory action of the pancreas.** *Ibid* **60**, 365-70.—The pancreas and intestinal contents of white rats, from which the thyroids have been removed 3 days to 2 weeks previously, contain decidedly less amylase than is found in the controls. It is concluded that the thyroid hormone acts as a non-sp. stimulus generally upon various physiol. functions of the animal. J. F. LYMAN

**Placental permeability. II. Localization of certain physiological activities in the chorionic ectoderm in the cat.** R. S. CUNNINGHAM. *Am. J. Physiol.* **60**, 448-60 (1922).—The different permeabilities of the cat fetus to  $\text{Na}_2\text{Fe}(\text{CN})_6$  and to ferric ammonium citrate (*C. A.* **95**, 1344) may be due to a sp. regulatory mechanism in the chorionic ectoderm which is normally concerned with the control of the passage of Fe-contg. substances, the decompn. of which is necessary for the prepn. of Fe for fetal use and storage. J. F. LYMAN

**Conditions of activity in endocrine glands. IX. Further evidence of nervous control of thyroid secretion.** W. B. CANNON AND P. E. SMITH. *Am. J. Physiol.* **60**, 476-95(1922); cf. *C. A.* **16**, 1802.—Stimulation of the thyroid gland by massage or through the cervical sympathetic trunk in the cat with denervated heart causes an increase in pulse rate amounting to as much as 25% in some cases. This is taken as evidence that the thyroid can be stimulated to produce its stimulatory hormone. **X. The cardio-accelerator substance produced by hepatic stimulation.** W. B. CANNON AND F. R. GRIFFITH. *Ibid* **60**, 544-50.—Further expts. on the effects of stimulating the hepatic nerves in an animal with denervated heart (*C. A.* **16**, 956) lead C. and G. to conclude that a substance of special and unknown nature, which increases the rate of the denervated heart and raises blood pressure, is discharged into the blood stream when the hepatic nerves are stimulated. J. F. LYMAN

**The relations of carbon dioxide in acidified blood.** T. R. PARSONS AND W. PARSONS. *J. Physiol.* **56**, 1-18(1922).—The sudden increase of  $\text{CO}_2$ -combining power observed by Straub and Meier (*C. A.* **13**, 460) in whole acidified blood at a certain reaction is not confined to the corpuscles but is also shown by the plasma. Four of these sudden inflections occur, viz., at  $15^\circ$  at  $p_{\text{H}}$  6.88, 6.73, 6.61 and 6.48. The first 2 inflections may be explained as due to the formation of  $\text{NaHCO}_3$  from Na obtained from the oxyhemoglobin mol., the remaining inflections may be due to a similar formation of  $\text{NaHCO}_3$ , or to the formation of a bicarbonate of hemoglobin. Hemoglobin is to be regarded as a multivalent colloidal ampholyte capable of giving rise to ions of various valencies in soln. J. F. LYMAN

**Maximum work and mechanical efficiency of human muscles, and their most economical speed.** A. V. HILL. *J. Physiol.* **56**, 19-41(1922).—App. is described for measuring the max. work of human muscles (biceps and anticus). The total energy ( $H$ ) set free in a maximal contraction of duration ( $t$ ) is given approx. by the relation  $H = 2W_0(1-bt)$ , where  $W_0$  is the energy value of external work ( $W$ ) + work done in overcoming the viscous resistance of the muscle to its change of form, and  $b$  is about 0.5. From this the mech. efficiency  $W + H$  may be calcd. as a function of the duration of the contraction, and it is shown that there is a certain optimum speed of movement, below which the efficiency falls slowly, and above which it falls rapidly. J. F. LYMAN

**Reaction of resting and active muscle.** A. D. RITCHIE. *J. Physiol.* **56**, 53-57 (1922).—The method used was to measure the difference of elec. potential between a resting and active muscle by means of  $\text{MnO}_2$  electrodes. There was no appreciable change in  $p_{\text{H}}$  concn. of frog muscle during moderate activity. J. F. LYMAN

**Relative excretion of urea and some other constituents of the urine.** E. B. C. MAYRS. *J. Physiol.* 56, 58-68(1922).—Sulfate, phosphate and creatinine occur in the urine in approx. the same ratio as in the circulating blood, while the urea is relatively less abundant in the urine than in the blood. The exptl. evidence is regarded as supporting the theory of reabsorption in the tubules rather than of tubule secretion.  
J. F. L.

**Regulation of the general circulation rate in man.** C. G. DOUGLAS AND J. S. HALDANE. *J. Physiol.* 56, 69-100(1922).—During rest about 5 to 8 l. of blood per min. passed through the lungs in different men, and during the hardest work the estd. flow was 24 l. per min. The rate of blood flow through the different tissues is, as a rule, so regulated that the pressure of  $O_2$  and the  $pH$  remain approx. const. round the tissue elements in each tissue. The rise in  $CO_2$  pressure and fall in  $O_2$  pressure in the mixed venous blood during muscular work are due mainly to the facts that blood coming from muscles has normally a low  $O_2$  pressure and high  $CO_2$  pressure and that during exertion the mixed venous blood contains a much higher proportion of venous blood from muscles.  
J. F. LYMAN

**The influence of X-rays on the properties of blood.** R. G. HUSSEY. *J. Gen. Physiol.* 4, 511-6(1922).—Massive doses of X-radiation caused a disturbance in the  $BA/H_2A$  ratio of the plasma of rabbits as shown by the decrease in  $C_H$  and the increase in  $CO_2$  values. The change is apparently due to a state of uncompensated alkali excess. The time required for the max. change in chem. reaction in the blood (about 3 hrs.) was also that required for the max. reduction in white blood cells. When  $NaHCO_3$  was injected into the peritoneal cavity results identical with those which followed X-ray exposure were obtained. The max. change in the latter case, however, occurred in a shorter time. This analogy between the effect of salt and X-rays is being further studied.  
CHAS. H. RICHARDSON

**Entero-hepatic circulation of the biliary acids.** H. WERTHEIMOR. *Compt. rend.* 174, 564-6(1922); cf. Foster *et al.*, *C. A.* 13, 1873.— $BaCl_2$  produces only a slight cloudiness in dog bile but a thick ppt. of hyoglycocholates in pig bile. In a chloralosed dog of 5 to 8 kg. wt., the cystic duct was ligated and a canula was introduced into the biliary duct. A glass tube was introduced into the duodenum for the injection of pig bile, the pyloric end of the stomach was ligated and the abdominal walls were closed but for the 2 canulae. Bile from the biliary duct was collected during 10 min. periods. After 2 samples were thus collected there was injected 120 to 150 cc. pig bile into the duodenum and the flow from the biliary duct collected in sep. portions to each of which was added 5 or 6 drops  $BaCl_2$  (33 g. to 100 g.  $H_2O$ ). In about the 3rd sample and thereafter  $BaCl_2$  produced ppts. which gave the reactions of Pettenkofer. The results of the expt. remain the same following the ligation of all branches of the hepatic artery. The elimination of the biliary acids is exclusively by the intermediary of the portal vein.  
L. W. RIGGS

**Intervening mechanism in the fixation of fats by the adrenal cortex.** A. POLICARD AND JULIANA TRITCHKOVITCH. *Compt. rend.* 174, 960-1(1922).—Expts. with mice were made by adding scarlet red to their food and detg. the presence of fats in the tissues by the usual histological methods. The fixation appears to be made directly from the fat in the blood without a previous destruction of the fat, the adipose vacuoles of the cell being surrounded with a very thin protoplasmic envelope and in very close contact with the blood carrying fat particles. The mechanism appears identical with that of the sebaceous glands. The conclusions of Ponomarew (cf. *C. A.* 8, 3323) are confirmed.  
L. W. RIGGS

**Maximum respiration at very high altitudes.** RAOUL BAYEUX. *Compt. rend.* 174, 1037-9(1922); cf. *C. A.* 15, 1562.—Max. respiration represents the greatest vol.

of instantaneous air that a subject is capable of delivering *in one sec.* There is a max. inspiration and a max. expiration. These 2 quantities may be equal or unequal according to the condition of the subject of the test. B., who has had 25 years of mountain climbing, had an av. max. inspiration of 400 centiliters and an av. max. expiration of 350 cl. at Chamonix. Both figures decreased on ascending Mt. Blanc and at the observatory (4370 m.) were about 315 and 275, resp. Subcutaneous injections of O resulted in a rise of both figures and the vol. of expiration approached more nearly that of inspiration. In a second subject the figures ranged 10 to 20% less. On return to the base of the mountain the max. respiration exceeded that before ascension.

L. W. RIGGS

**Kidney function.** A. N. RICHARDS. *Am. J. Med. Sci.* **163**, 1-19(1922).—A study of glomerular function made by direct observation supports the filtration hypothesis. Increased urine formation is associated with an increase in blood pressure, uncomplicated by an increase in the velocity or vol. of blood flow in the kidney. Nervous stimuli and chem. substances may exert diff. degrees of effective influence upon the afferent and efferent vessels of the glomerulus. This may be a factor in that automatic regulatory control of glomerular filtration which is responsible in part for the maintenance of constancy of blood compn. The number of glomeruli showing active circulation may be changed by the injection into the circulation of such substances as physiol. saline, hypotonic saline or  $\text{Na}_2\text{SO}_4$ , urea, glucose, caffeine, adrenaline, and pituitrin.

G. H. S.

**Heat regulation and protein exchange.** HERMANN FREUND. *Arch. expl. Path. Pharm.* **88**, 216-26(1921).—Dogs on a known N balance were given antipyrine or morphine and coincident with the period of reduced temp. there was a considerable increase (30 to 70%) in the elimination of urinary N.

G. H. S.

**Specific effects of substances derived from individual organs. III.** E. ABDERHALDEN AND E. GELLHORN. *Arch. ges. Physiol. (Pflüger's)* **182**, 28-49(1920).—Optones (the hydrolyzed products of tissues) prepd. from corpus luteum and from testis possessed a mydriatic action on the enucleated frog eye. They also caused diastolic arrest when added to a heart prepn. Thus they appear to belong to the group of parasympathetic paralyzing substances. Thyroid and hypophysis optones exert a myotic effect and show almost no effect on heart action. Thyimus optone is mydriatic; ovarian and anterior lobe of the hypophysis optones stimulate adrenaline mydriasis. When mixts. of myotic and mydriatic optones are used the mydriatic effect usually dominates; only in mixts. of thyroid and testis optones is the myotic effect the more intense. **IV.** E. ABDERHALDEN AND N. SCHIFFMANN. *Ibid* **183**, 197-209(1920).—Tadpoles were fed thyroid and exts. of hydrolyzed thyroid. The effects of the exts. were comparable to those induced by thyroid. The endocrine glands of the tadpoles were studied but no specific effects associated with the feeding could be demonstrated.

G. H. S.

**Utilization of oxygen by muscle under reduced oxygen supply.** F. VERZAR. *Arch. ges. Physiol. (Pflüger's)* **183**, 239-52(1920).—With regard to their dependence upon O tension all mammalian tissues can be divided into two groups (1) facultative oxybiotic, and (2) obligate oxybiotic tissues. Muscle belongs in the first group. Thus when the O tension of the blood is reduced, or during circulatory disturbances, or in anemia, the amt. of O utilized by the muscle is decreased.

G. H. S.

**Cause of the heart beat.** C. MANSFELD AND A. V. SZENT-GYÖRGYI. *Arch. ges. Physiol. (Pflüger's)* **184**, 236-64(1920).—The expts. were conducted upon the hearts of mammals as well as upon those of cold-blooded animals. The significance of  $\text{CO}_2$  as a stimulus of the heart beat is demonstrated by perfusion expts. in which the perfusion fluid is such that it will or will not fix  $\text{CO}_2$ . When the fluid contains  $\text{NaOH}$ ,  $\text{Ca(OH)}_2$ ,  $\text{Ba(OH)}_2$ ,  $\text{NH}_4\text{OH}$ , or  $\text{Na}_2\text{CO}_3$  retardation of rhythm, followed by arrest,



results. The OH-ion concn. has no bearing on this effect, since alkalis such as  $\text{NaHCO}_3$ ,  $\text{Na}_2\text{HPO}_4$ , which do not fix  $\text{CO}_2$ , do not affect the rhythm even when used in ten-fold concns. The acapnic effect is upon the automatic tissue, the elec. or mechanical excitability of which is not altered by the change. Thus  $\text{CO}_2$  is not simply a condition for, but is indeed the stimulus of, heart activity. The acapnic heart is restored to normal activity by Ringer soln. contg. 0.002  $N$   $\text{CO}_2$ . Free  $\text{CO}_2$  in the Ringer soln. causes a marked acceleration of heart activity. The H ion is also of significance but even in neutral solns.  $\text{CO}_2$  is effective. With the mammalian heart rendered acapnic with alk. Ringer soln. activity is restored if the perfusion fluid contains 0.002  $N$  free  $\text{CO}_2$  and is introduced into the right auricle. G. H. S.

**Effect of hydrogen-ion concentrations upon blood vessels.** EDGAR ATZLER and GUNTHER LEHMANN. *Arch. ges. Physiol.* (Pflüger's) 190, 118-36(1921).—Solns. of varying  $p_H$  were perfused through the vessels in frogs. With values between 5 and 7 the perfusion rate remained unchanged. When the  $p_H$  was below 5 or above 7.1 vasoconstriction resulted. The results were essentially the same whether the central nervous system was intact or not. G. H. S.

**Surviving red and white muscle of the rabbit.** O. RIESSER. *Arch. ges. Physiol.* (Pflüger's) 190, 137-57(1921).—The contraction curves of the red and white muscle of the rabbit were recorded. The portions of muscle, extensor communis (white) and semitendinosus (red), were suspended in oxygenated Locke soln. The two types of muscle could always be differentiated in that the red muscle invariably produced a contraction curve with a second peak on the descending limb. A similar peak was present in the curve of contraction for the white muscle when it had been subjected to veratrine. This compd. has but little effect either upon the form or extent of the contraction of red muscle. With white muscle physostigmine has but slight effect whereas with the red muscle it causes a very characteristic prolonged contracture of the descending limb of the curve. With red muscle in slight contracture  $\text{NH}_3$  produces a more intense but reversible contracture, but upon white muscle, even in multiple quantities it is almost without effect. In a note on the vegetative innervation of skeletal frog muscle it is stated that the gastrocnemius is thrown into contraction in Ringer soln. in the presence of 1:200,000 to 1:100,000 acetylcholine. Atropine or novocaine, 1:1000, removes the contracture. Preliminary treatment of the muscle with atropine prevents the acetylcholine from manifesting its activity. Nerve-free muscle is not affected by acetylcholine. Although curarizing the animal does not inhibit the action of acetylcholine the treatment of the isolated muscle with curare is inhibitory. G. H. S.

**The local galvanic reaction of the skin: local stimulation and electrical conductivity.** U. ЕВВСКЕ. *Arch. ges. Physiol.* (Pflüger's) 190, 230-69(1921).—Skin cond. to galvanic currents is reduced by mechanical, thermal, elec. and chem. (acids, alkalis, narcotics) stimuli. G. H. S.

**Hydrogen-ion concentration in the regulation of respiration.** ALFRED FLEISCH. *Arch. ges. Physiol.* (Pflüger's) 190, 270-79(1921).—Rabbits were given slow intravenous infusions of  $\text{NaH}_2\text{PO}_4$  and measurements of the respiration, and the  $\text{CO}_2$  tension and the H-ion concn. ( $C_H$ ) of the arterial blood were made for comparison with similar titrations made prior to the infusion. The relative values indicated that the ventilation was increased, the  $C_H$  was increased but the  $\text{CO}_2$  tension was decreased by the acid infusion. It therefore appears that respiration is regulated by the  $C_H$  of the blood or of the respiratory center rather than by the  $\text{CO}_2$  tension. Cf. C. A. 16, 585. G. H. S.

**Preservation of functions in cells by substitution of the free oxygen by chemical compounds: "Pseudoanoxibiosis." III. Spermatozoa.** WERNER LIPSCHITZ and

GÜNTHER HERTWIG. *Arch. ges. Physiol.* (Pflüger's) **191**, 51-9(1921).—The exposure of frog spermatozoa to O for 1-3 hrs. results in complete death of the cells. The change which accompanies the loss in motility and the loss in reducing property is an irreversible action. Under anaerobic conditions (exposed to H) the cells also lose in motility but this change is restored by the addition of an easily reducible nitro group, as dinitrobenzene. Even in low concn. HCN is inhibitory of the motility but the cells are still capable of causing reduction. Both fumaric and malic acids are toxic, the latter being the more active.

G. H. S.

**Energy transformation in muscle. V. Lactic acid formation and mechanical work.** OTTO MEYERHOF. *Arch. ges. Physiol.* (Pflüger's) **191**, 128-83(1921); cf. *C. A.* **15**, 2307, 3310.—With the frog gastrocnemius muscle suspended in a H atm. or in Ringer soln. the lactic acid fatigue max. is about 0.35% when stimulated by single induction shocks. If the  $p_H$  of the Ringer soln. is changed by the addition of alkali to  $P_H$  10 the figure is raised to 0.5%. In the last case the anaerobic work done is considerably increased, although the isometric lactic coeff. (Km) is somewhat decreased. Approx. 20% of the lactic acid appears in the alk. Ringer soln., whereas in neutral or but weakly alk. solns. only 5% of the lactic acid is found. Direct alkalinization of the muscle by the *in vivo* ingestion of a soda soln. has no effect on the lactic acid max. When suspended in a weakly acid soln. the value is but slightly decreased. These observations prove that the fatigue max. is associated with the lactic acid content of the muscle. The isometric coeff. falls perceptibly in the course of anaerobic fatigue. During the second half of the fatigue it is one-third less than during the first half. Submaximal shocks do not greatly disturb the coeff. Narcotics and alc. greatly reduce the Km. Tetany also results in a decreased Km. The work coeff. (derived from the work done and the lactic acid produced) should be about 8.2 but it actually is somewhat less, being modified by the degree of the fatigue and the temp. The oxidative efficiency is about one-half of the anaerobic. Apparently the maximal potential energy developed in a muscle by stimulation is never greater than 75% of the total energy change. These findings were confirmed qualitatively upon the guinea pig gastrocnemius. G. H. S.

**Rigor mortis.** HANS WINTERSTEIN. *Arch. ges. Physiol.* (Pflüger's) **191**, 184-5(1921).—When kept in an environment of N or of H frog muscle develops rigor, but in O-free Ringer soln. rigor does not occur. The presence of lactic acid in the solns. suggests that rigor is associated with the formation of this acid.

G. H. S.

**Resolution of rigor and its relation to the swelling and coagulation of the muscle protein.** HANS H. WEBER. *Arch. ges. Physiol.* (Pflüger's) **191**, 186-98(1921).—Shrinkage in the muscle can in no way explain the resolution of rigor, a process apparently due solely to a rupture of the contractile elements following an accumulation of lactic acid.

G. H. S.

**Creatine content of frog muscle in hypnotic rigor.** HERBERT SCHÖNFELD. *Arch. ges. Physiol.* (Pflüger's) **191**, 211-16(1921).—After 3 hours of rigidity there was an increase in creatine of about 21%. The av. values were 3.663 as compared with 3.013 for the normal muscle.

G. H. S.

**The decomposition of carbohydrate in striated muscle. I.** F. LAQUER. *Z. physiol. Chem.* **116**, 169-222(1921).—In spring and summer frogs the lactic acid found was equiv. to the glycogen and lactacidogen contents. In winter frogs, kept for several days at 22-27°, the lactic acid found exceeded the glycogen and lactacidogen contents. The precursor for the excess is designated as "intermediate carbohydrate." At 45° muscle converts glycogen, starch and hexosephosphate to lactic acid; it does not convert maltose, dextrose and levulose. Phosphate is necessary for the conversion; bicarbonate cannot replace it. At 30° dextrose and levulose are lactic acid formers. It is suggested that the difficulty in diabetes lies in the inability to form the "intermediate

carbohydrate." For the lactic acid derivs. the method described in Abderhalden's *Arbeitsmethoden* 5, 1254 was adapted as a micro-method. Two-10 mg. could be estd. within 95-97%.  
R. L. STEHLE

**Chemical nature and transformations of blood fat.** I. LIPSCHÜTZ. *Z. physiol. Chem.* 117, 212-7(1921).—The compn. of some samples of blood fat may differ as much as shown by the following analyses: unsaponifiable matter 30-50% to 48-50%; cryst. cholesterol in percentage of unsaponifiable matter 88% to 58-60%; amorphous cholesterol oxidation products in percentage of unsaponifiable matter 12% to 40-42%; cholesterol content (calcd. to cholesterol ester basis) in percentage of total fatty matter 63.6% to 90.9%; true fat 36.4% to 9.1%. L. interprets these variations to indicate the formation of cholesterol from oleic acid, bile acids being the ultimate product.  
R. L. S.

**Effect of potassium and radioactivity on the rate of oxidation of erythrocytes.** P. ELLINGER. *Z. physiol. Chem.* 116, 266-76(1921).—The object was to test Zwaardemaker's hypothesis that the physiol. action of K is due to its radioactivity. When red cells (bird) were suspended in K-free Ringer soln. the rate of oxidation diminished about 1/3. K-rich Ringer soln. caused an increase in the rate. Rb but not Cs could be substituted for K. Radioactive materials (U and Th compds.), Th emanation and Ra emanation in amts. similar to those employed by Zwaardemaker could not replace K.  
R. L. STEHLE

**Decomposition products of cholesterol in animal organs.** X. I. LIPSCHÜTZ. *Z. physiol. Chem.* 117, 201-11(1921).—After the removal of cholesterol from the blood 2 groups of substances closely related to cholesterol were obtained. The first was pptd. with digitonin and consisted largely of oxysterol digitonide. On dissolving in AcOH and adding H<sub>2</sub>SO<sub>4</sub> the soln. showed absorption lines in the red, yellow and green and between the green and blue. The first 2 bands disappeared after adding CHCl<sub>3</sub>. This shows the presence of oxysterol and dioxysterol. The material not pptd. with digitonin gives a strong cholesterol reaction and appears to contain 3 additional oxidation products of cholesterol.  
R. L. STEHLE

**Influence of the spleen upon digestion.** W. MOLLOW. *Z. physiol. Chem.* 117, 218-39(1921).—No influence upon the secretions of the stomach, pancreas and liver could be detected in animals with gastric and intestinal fistulas.  
R. L. STEHLE

**The physiological significance of the change in permeability of muscle fiber membrane.** G. EMBDEN AND E. ADLER. *Z. physiol. Chem.* 118, 1-49(1922).—Gastrocnemius muscles contained in Ringer soln. give off more H<sub>2</sub>PO<sub>4</sub> to the medium when they are active than when at rest. The greater the fatigue produced the greater is the amt. of H<sub>2</sub>PO<sub>4</sub> given up. When fatigued by contraction in O and placed subsequently in Ringer soln. the result is especially marked. The results noted may be due to increased permeability of the muscle membrane. To test this view cane sugar soln. was substituted for Ringer soln. whereupon an increased H<sub>2</sub>PO<sub>4</sub> excretion was observed. Contraction at higher temps. gives similar results.  
R. L. STEHLE

**Influence of lack of oxygen on the permeability of muscle fiber membranes.** M. SIMON. *Z. physiol. Chem.* 118, 96-122(1922).—Deprivation of O caused an increased elimination of H<sub>2</sub>PO<sub>4</sub> from the muscle. This is regarded as due to increased membrane permeability.  
R. L. STEHLE

**Potassium paralysis.** H. VOGEL. *Z. physiol. Chem.* 118, 50-95(1922).—Paralysis of the muscle caused by K<sub>2</sub>SO<sub>4</sub> soln. is accompanied by a decrease in H<sub>2</sub>PO<sub>4</sub> elimination (cf. preceding abstr.). This indicates a condition of decreased permeability and various expts. support such a view.  
R. L. STEHLE

**Influence of chemical composition and physico-chemical structure on the function of frog muscles.** H. BEHRENDT. *Z. physiol. Chem.* 118, 123-67(1922).—The gastrocnemius was compared with the semimembranosus and gracilis of the same animal with

regard to content of lactacidogen, free  $H_2PO_4$ , "rest  $H_2PO_4$ ", and glycogen but no differences sufficient to explain the functional capacities were found. The gastrocnemius and semimembranosus were then compared with regard to  $H_2PO_4$  excretion and the effect of sucrose, K salts and lack of O on permeability, fatigue and recovery. R. L. S.

The endocrine organs (DRYERRE) 17.

MILROV, J. A. and MILROV, J. H.: *Practical Physiological Chemistry*. 3rd Ed. revized. Edinburgh: W. Green & Sons, Ltd. 449 pp. 21s. Reviewed in *Nature* 109, 704(1922).

### G—PATHOLOGY

H. GIDEON WELLS

**Specific fixative property in the serum of pregnant women.** G. IZAR. *Biochim. e terapia sper.* 8, 353-5(1921).—Distd.  $H_2O$  added to a mixt. of serum and glycerol ext. of (dehydrated) placenta produces a ppt. which, after washing and centrifuging, possesses specific power of complement fixation. H. W. BANKS, 3RD

**Researches on the value and on the nature of the urinary reaction of Sgambati, in acute peritoneal infections.** G. MARCIALIS. *Biochim. e terapia sper.* 9, 102-119 (1922).—The reaction of Sgambati (*Il Policlinico, Sezione Pratica*, no. 9, 1920) is found to be specific for acute peritoneal infections. It depends on the formation of a blue-gray ring upon careful addition of fuming  $HNO_3$  to urine in a test-tube, without mixing the two layers. After mixing and allowing to stand for several hrs. a bright ruby red color is extd. with  $CHCl_3$ . A great no. of cases were studied, and the results of the first (blue-gray layer) and second (red with  $CHCl_3$ ) reactions are given for 40 different diseases and pathological conditions. The method has great prognostic and diagnostic values. The latter is especially due to the second phase of the reaction. It is supposed that this is due to aromatic chromogens and their oxidation products which are found in those suffering from peritonitis, and that these products are in a state easily to be extd. with  $CHCl_3$ . H. W. BANKS, 3RD

**Electrochemical research on cancer.** N. WATERMAN. *Nederland Tijdschr. Geneeskunde* 66, 1780(1922).—Small pieces of human tissue, which are perfused with various isotonic salt solns., are contained in a narrow tube, open at both ends. Their elec. cond. is measured by means of Wheatstone's bridge method. In the same measurement the polarization is detd. according to a method described by Wien by connecting a variable self-induction coil in the circuit. Normal tissue, as a rule, exhibits a larger elec. resistance and also a larger polarization than cancerous tissue. If normal tissue is first perfused with Ringer soln. and then with isotonic  $CaCl_2$  soln. both the elec. resistance and the polarization decrease. If cancerous tissue is treated in the same way the opposite phenomenon is observed, i. e., the elec. resistance and the polarization increase. Cf. *C. A.* 15, 3137. R. BEUTNER

**The suspension stability of the blood.** R. FÄHRJES. *Acta Medica Scand.* 55, 228; *Physiol. Abstracts* 6, 186.—Blood sedimentation is thoroughly discussed. The increased sedimenting velocity of blood in pregnancy and in certain diseases is due chiefly to increased agglutination and to a diminished number of corpuscles. Agglutination is dependent on the properties of the plasma, which are fully discussed; the chief one appears to be an increase in the globulin content. Under some conditions there may be a tendency to sedimentation *in vivo*. H. G.

**Precipitins and complement-fixation substances.** R. BRUVNOGHE. *Compt. rend. soc. biol.* 82, 951(1919); *Abstracts Bact.* 4, 80.—The question of the identity of precipitins and complement-fixing substances was examd. The results appear to favor the duality of the two substances. H. G.

**Renal efficiency and hyperglucemia.** L. A. I. MAXWELL. *Med. J. Australia* 7,

551-3(1920); *Physiol. Abstracts* 6, 142.—Renal inefficiency was present in 58% of the diabetics examd.; this factor must be taken into account in blood-sugar estns. In  $\frac{4}{5}$  of the cases the blood showed increased concn. Lipemia was not a marked feature.

H. G.

**The technic of Kaup's modification of the Wassermann reaction.** M. SERN AND H. DANZIGER. *Z. Immunität.* 28, 377-400(1919); *Abstracts Bact.* 4, 162.—Kaup's modification of the Wassermann reaction was devised for the purpose of making quant. measurements of complement fixation. The usual anti-sheep red corpuscle hemolytic system is used, with guinea pig serum as complement. Two preliminary titrations are carried out. In one of these, const. quantities of 10% complement are used with decreasing quantities of amboceptor. The red cells are then sensitized with 4 units of amboceptor, and the complement is titrated against these sensitized cells. In this second series the complement is titrated in the presence of antigen (ext.), normal serum and a mixt. of normal serum and the antigen. The minimal dose of complement effective in the presence of both normal serum and antigen is thus detd. The antigen is carefully titrated for its anticomplementary and hemolytic action, and to det. the zone of diln. in which the antigen exhibits complete and most frequent binding with positive syphilitic sera. When the test is carried out with careful attention to the preliminary titrations and controls, it yields more const. results and a greater number of positive reactions than are obtainable by application of the original Wassermann method to the same sera. Comparative results on several hundred sera are presented. Antigens made from normal heart muscle were found to be as useful as any of the so-called specific syphilitic exts. Paradoxical reactions of sera, which were found to be positive on one day and negative later, were attributed to phys.-chem. changes in the sera. H. G.

**The thromboplastic shock in birds.** P. NOLÉ. *Arch. intern. physiol.* 17, 271-336 (1922).—Roosters were used in the expts. When bird plasma is coagulated by  $\text{CHCl}_3$  the liquid pressed out is toxic to birds, even when freed of  $\text{CHCl}_3$ . When the ext. is injected into a vein the animal dies of general thrombosis. If the expressed liquid is given more slowly it produces a marked diminution of coagulability which is accompanied at times by intravascular hemolysis and depression of arterial tension. These reactions are more marked if the serum is rich in thrombin, which leads to the conclusion that they are the response of the organism to the intravenous injection of thrombin contained in abundance in the  $\text{CHCl}_3$  serum. The incoagulability of the blood is not an augmentation in plasma content of anti-thrombin, but rather a diminution of the mother substances of fibrin and thrombin. Preliminary extirpation of the liver does not change the response in any essential particulars. The serum of the plasma or the blood has a strong neutralizing effect with respect to the coagulating and toxic properties of the  $\text{CHCl}_3$  serum. Plasma or serum satd. with  $\text{CHCl}_3$  produces, on intravenous injection a profound shock by direct paralysis of the vascular system. The toxicity is due to the protein  $\text{CHCl}_3$  complexes. F. S. HAMMETT

**The separation of antithrombin and passive immunization against protein intoxication.** H. DEWAELE. *Arch. intern. physiol.* 19, 33-73(1922).—When incoagulable plasma obtained from a dog during the antithrombic phase which follows the intravenous injection of peptone is added to normal fresh blood, the latter is made incoagulable, even if heterogenous. This principle resists  $100^\circ$ . When by moderate diln. of the plasma, a fibrous coagulum is produced, the active agent passes into the filtrate. Active immunity is retained as long as the blood is incoagulable and even a bit longer because of the cellular immunity. Nevertheless the incoagulable plasma does not confer passive immunity. On the other hand when a coagulum of fibrin is spontaneously produced in such a plasma, the liquid part (spontaneous seroplasma) does confer passive immunity. When the fibrinous coagulum is sepd. by heating to  $56^\circ$  the filtrate does not

confer passive immunity unless reactivated by complement. The same is true of incoagulable plasma heated to 100°. Spontaneous seroplasma, the seroplasma obtained at 100° reactivated, and the dild. seroplasma confer immunity when given by mouth, or by any other way and are effective homologously or heterologously. The immunity is sp. for the original peptone.

F. S. HAMMETT

**Fibrinolysis. III.** M. ROSENMAN. *Biochem. Z.* **129**, 101-10(1922).—A continuation of the earlier reported studies. R. isolated a substance from pleuritic exudates which retards fibrinolysis. It is characterized by being pptd. by alc. and half satn. with  $(\text{NH}_4)_2\text{SO}_4$  by its non-dialyzability, its soly. in distd.  $\text{H}_2\text{O}$  and inactivation at 60° to 65°. It may be the same as the substance present in serum which retards fibrinolysis, although the identity is not proved. The substance occurs also in considerable amt. in the lungs, thyroid and kidneys; in massive quant. in the liver and in traces in the heart muscle. It is increased in the pleuritic exudates of tuberculous individuals. But little antithrombolysin is present in ascitic fluid and practically none in transudate, cerebrospinal fluid and edema liquids. The thromboligin of the serum varies with the individual and with various pathol. processes. When a pleural exudate is inactivated at 46 to 48° its antifibrinolytic action increases. The pleural exudate of tubercular individuals contains a fibrinolytic substance also. Fibrinolysis is retarded by  $\text{CHCl}_3$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{ZnCl}_2$ , acids and alkalis.  $\text{CHCl}_3$  produces a turbidity in the thrombolysin soln. while the other compds. cause pptn. in the presence of salts. A well washed fibrin prep. goes into soln. by autolysis or by fibrinolysis more rapidly than a sample of fibrin of the same age but not so well washed.

F. S. HAMMETT

**The action of phlorhizin on the blood sugar in diffuse bilateral hematogenous nephritides.** A contribution to the question of the action of phlorhizin. S. HETÉNYI. *Biochem. Z.* **129**, 183-6(1922).—A tabular presentation of the effect of phlorhizin injections on a series of patients with kidney disorders. Blood and urinary sugar, blood pressure and concn. were detd. In one group of cases the blood sugar fell and glucosuria was produced. In the other group the blood sugar rose and no marked glucosuria appeared. The results show that the drug does not act on the kidneys alone. In normal conditions the sugar mobilization effect is marked; in these pathol. conditions it is exposed.

F. S. HAMMETT

**Refractometric studies of the reactions between isolated cancer cells and blood serum. II.** R. KORIYCHONER. *Biochem. Z.* **129**, 605-19(1922); cf. *C. A.* **14**, 2656.—When carcinoma cells were added to sera from 22 non-febrile carcinoma-free individuals the refractive index ( $n$ ) was increased. When similar cells were added to sera from 20 non-febrile carcinomatous patients the  $n$  was diminished. In the sera from 7 out of 8 patients with fever but without carcinoma the  $n$  sank. When the sera from 22 carcinoma and fever-free patients and from 20 carcinomatous non-febrile patients were heated to 60° the addn. of carcinoma cells caused reversion of the  $n$  in 13 of the former and 14 of the latter, while in 7 out of 8 febrile carcinoma-free sera no change occurred. Almost exactly the same ratios were found in reaction change when 2% NaCNS was added. Simultaneous inactivation and addn. of NaCNS to the serum both before and after inactivation gave indeterminate results. When sera from 6 carcinoma- and fever-free individuals and 6 carcinomatous fever-free patients were allowed to stand for 14 days the reaction was reversed in 5 of the former and 4 of the latter. In 4 febrile non-carcinomatous patients it was not changed. When such sera were inactivated or treated with NaCNS there usually occurred a reversal of the reaction.

F. S. HAMMETT

**Urine examination as an index of renal disease.** H. W. JONES. *N. Y. Med. J.* **115**, 531-3(1922).—The estn. of the d. of urine is one of the most if not the most important part in urine examn. The functional tests are considered superior diagnostic measures to the usual urine analyses.

F. S. HAMMETT

**Worthwhile tests of kidney function.** M. F. MORRIS. *N. Y. Med. J.* 115, 538-90 (1922).—M. believes that the phenolsulfonephthalein test, the 2-hr. test, with measurement of fluid intake and output, salt and N and chem. analysis of the blood yield results leading to better diagnosis.

F. S. HAMMETT

**A contribution to the etiology of feeble-mindedness with special reference to prenatal enamel defects.** L. PIERCE CLARK AND C. E. ATWOOD. *N. Y. Med. J.* 115, 573-9(1922).—The defective enamelization of teeth is a gross teratological fault. It may have a metabolic or a maternal infectious process as its origin. Defective enamel in a questionable feeble-mindedness is not of immediate diagnostic moment.

F. S. HAMMETT

**The urea concentration test for kidney function.** E. WEISS. *Penn. Med. J.* 25, 607-13(1922).—Report of the use of the test in various pathol. conditions of the kidney. A favorable opinion of its usefulness is given.

F. S. HAMMETT

**The effect of treatment with artificial high altitude sunlight (Hohensonne) on the antitryptic titer of the blood.** HARRY KOENIGSFELD. *Klin. Wochschr.* 1, 58(1922).—Twenty-six people were treated with rays from a Bach (Hohensonne) app. The antitryptic titer of the blood and a complete blood count were made in each case. Short treatments always increase the number of polymorphonuclear leucocytes (P. L.) and frequently increase the number of large mononuclear leucocytes. The antitryptic titer is decreased. Long or repeated treatments give rise to a rapid decrease in the number of P. L., a slow decrease in the number of large mononuclears and an increase in the number of lymphocytes. Under these conditions the antitryptic titer is markedly increased. The authors conclude that the changes in the antitryptic titer of the blood after illumination are not produced directly by the illumination but are secondary to the changes produced in the number of P. L. In the initial stages of the destruction of these cells, proteolytic enzymes are liberated. These combine with the antitrypsin of the plasma and so temporarily reduce the antitryptic titer. The liberation of the proteolytic enzymes, however, calls forth an increased production of the antitrypsin which rapidly raises the antitryptic titer.

MILTON HANKE

**Transmissible lysis of staphylococcus and its therapeutic applications.** A. GRATIA. *Bull. acad. roy. méd. Belg.* [5] 2, 72-86(1922); cf. *C. A.* 16, 945.—The lytic agent, details for the prepn. of which are given, has the properties of the previously known "bacteriophages" and is rigorously specific. In various staphylococcus infections in man beneficial results were obtained with subcutaneous injections of 0.5 to 3 cc., but it cannot yet be considered established that the "phage" was actually the curative agent.

M. HEIDELBERGER

**Clinical observations on treatment and progress in diabetes.** F. M. ALLEN AND J. W. SHERRIL. *J. Metabol. Res.* 1, 377-434(1922).—A review of A.'s method of treatment and the results obtained, and of the newer treatments of Petren and of Newburgh and Marsh (cf. *C. A.* 15, 551, 2669).

W. A. PERLZWEIG

**The equilibrium between blood serum and serous cavity fluids.** R. F. LOEB, D. W. ATCHLEY AND W. W. PALMER. *J. Gen. Physiol.* 4, 591-5(1922).—Comparative studies of serum and ascitic or chest fluid from the same human individual suffering from certain pathological conditions showed: That the edema fluid contained more Cl and less K than the blood while the same concns. of Na, HCO<sub>3</sub>, Ca, urea, glucose, and non-protein N occurred in both.  $\Delta$  was the same in serum and edema fluid; the specific cond. of the edema fluid was higher. The variations between the serum and edema fluid appear to be related to the difference in protein concn. of the 2 solns., the % of protein always being higher in the blood serum. The relationships between blood serum and edema fluid seem to result from a simple membrane equil. which is influenced in part by the proteins present.

CHAS. H. RICHARDSON

**Zinc and cancer.** PAUL CRISTOL. *Compt. rend.* 174, 887-9(1922).—The analytical technic of Delezenne (cf. *C. A.* 13, 3197) was followed. In benign connective tissue tumors the Zn content was 0.294 to 0.307 parts in 1000 of dry matter. The central portion of one of these tumors, in which sarcomatous degeneration had commenced, contained 0.369. Malignant epithelial tumors contained 0.424 to 0.794 parts of Zn in 1000 parts of dry material. These results appear to show that the Zn content of cancerous tissues is a function of the cellular and nuclear activity.

L. W. RIGGS

**Experimental azotemia and hyperproteoglucemia.** H. BIERRY, F. RATHERY AND F. BORDET. *Compt. rend.* 174, 970-3(1922).—Expts. were made with dogs by an analysis of the blood before and after ligation of the ureters. Following the sudden suppression of urine excretion, a dog lives but 2 or 3 days and during this period the increase of protein sugar in the blood plasma is paralleled to an increase of the urea but less rapid and less intense. The amt. of protein sugar in the blood plasma of the dog with ligated ureters was nearly double that in case of the normal dog and the urea 4 to 8 times as great. With human nephritides the amt. of protein sugar may reach 3 times that for a normal person.

L. W. RIGGS

**Differentiation of the phenomena of shock by contact.** W. KORACZEWSKI. *Compt. rend.* 174, 1034-7(1922); cf. *C. A.* 14, 569 and A. Lumière, *C. A.* 15, 1165, 2123.—Expts. with guinea pigs led to the conclusion that there is an exptl. basis for distinguishing between the cellular or anaphylactic shock which requires a period of incubation, and a humoral shock which appears immediately. Among the humoral shocks are the flocculent, the lytic and the thromboplastic.

L. W. RIGGS

**In behalf of the stomach tube.** REGINALD FITZ. *J. Am. Med. Assoc.* 78, 1446-50 (1922).—An historical sketch of the use of stomach brushes and tubes is given. Expts. were made by detg. the free HCl following an Ewald meal in 28 normal medical students and in 12 patients who were operated on for gastric and duodenal ulcer and who were operated on later for gastrojejunal ulcer. HCl was also detd. in 20 cases of hyperacidity and stasis. The findings are discussed at length. The facts established are sufficient to demonstrate the importance of simple gastric analysis in the routine study of patients with gastric and intestinal symptoms.

L. W. RIGGS

**Relation between fatigue and the susceptibility of rats towards a toxin and an infection.** ELLA H. OPPENHEIMER AND REYNOLD A. SPAETH. *Am. J. Hyg.* 2, 51-66 (1922).—Apparently fatigue increases, rather than decreases, the resistance of rats to tetanus toxin, or to exptl. infection with the type I pneumococcus. Results of this type are obtained regardless of whether the fatigue period precedes or follows the injection.

G. H. S.

**Production of hemolysins and hemagglutinins in the domestic fowl.** R. R. HYDE AND C. E. BAILEY. *Am. J. Hyg.* 2, 246-53(1922).—Domestic fowls were treated with erythrocytes of the pigeon, sheep, guinea pig, ox and rabbit. In general the fowls failed to respond by antibody production as most animal species do. From *in vitro* expts. it appears that fresh chicken serum renders the red cells non-agglutinable.

G. H. S.

**Blood-sugar tolerance test as an aid in the diagnosis of gastrointestinal cancer.** JULIUS FRIEDENWALD AND G. H. GROVE. *Am. J. Med. Sci.* 163, 33-40(1922); cf. *C. A.* 15, 892.—The curve of sugar tolerance may offer a means of effecting a diagnosis and of differentiating malignant and benign diseases of the gastrointestinal tract. As contrasted with the blood-sugar curve in normal individuals after the ingestion of 100 g. of glucose the test made upon the blood of a patient with gastric carcinoma 2 hours after the administration remains high.

G. H. S.

**Skin tests with foreign proteins in various conditions.** F. M. RACKEMANN. *Am. J. Med. Sci.* 163, 87-100(1922).—A tabulation and discussion of the skin tests applied to 930 patients.

G. H. S.



**Enzyme mobilization by means of Röntgen-ray stimulation.** WM. F. PETERSEN AND C. C. SÆLHOF. *Am. J. Med. Sci.* **163**, 101-20(1922).—The dosage and the area exposed det. the effect. Moderate doses may stimulate the organs and result in a mobilization of various serum enzymes (protease, peptidase, lipase, diastase). Large doses decrease the titers. Irradiation of the hepatic area in dogs causes a transitory leucocytosis and eosinophilia, and an increased serum protease, peptidase, lipase, and diastase. Exposure of the intestinal area leads to a more persistent leucocytosis, a marked increase in peptidase, and smaller increases in the other enzymes. Exposure of the splenic area causes a diminution of the serum enzymes except lipase. Irradiation also reduces the blood coagulation time, increases the antienzymes, and has but little effect on temp. or complement titer. When the liver area is rayed the N excretion is increased. G. H. S.

**Nature and treatment of chronic nephrosis.** ALBERT A. EPSTEIN. *Am. J. Med. Sci.* **163**, 167-86(1922).—Chronic nephrosis is characterized, among other things, by oliguria and albuminuria, by the absence of marked N retention in the blood, by increased blood cholesterol, by a reduction of the total protein of the serum and by an inversion of the albumin-globulin ratio. It is suggested that nephrosis is a metabolic disease related to a state of hypothyroidism. G. H. S.

**Prevalence of free hydrochloric acid in cases of carcinoma of the stomach.** HOWARD R. HARTMAN. *Am. J. Med. Sci.* **163**, 186-90(1922).—Data collected on 551 patients show that achlorhydria is by no means const. in gastric carcinoma, since it was present in only 53.72% of the patients. About 2 in 5 cases showed free HCl. G. H. S.

**Röntgen-ray stimulation of the pancreas in experimental pancreatic deficiency.** WM. F. PETERSON AND C. C. SÆLHOF. *Am. J. Med. Sci.* **163**, 391-401(1922).—A transient increase in sugar output followed by an increase in sugar tolerance results from irradiation of the pancreatic region in exptl. pancreatic deficiency. Increased tolerance is not due to a preliminary sugar elimination. Usually a temporary increase in blood sugar is found. When acidosis is present at the time of irradiation this condition may be improved. In appropriate dosage the irradiation stimulates the cellular metabolic process of the pancreas. Too large doses injure the tissue and result in a diminution of the sugar tolerance. G. H. S.

**Experimental polyuria.** McMICKEN HANCHETT. *Am. J. Med. Sci.* **163**, 685-97(1922).—Exptl. lesions of the hypophysis alone did not regularly cause polyuria but when in addition there was traction upon the floor of the third ventricle polyuria always occurred and was somewhat proportional to the amt. of traction. In polyuria produced in this way intravenous injections of pituitrin temporarily reduced the excretory rate. Epinephrine was without effect. G. H. S.

**Significance of ion antagonism in hemolysis.** S. M. NEUSCHLOSZ. *Arch. ges. Physiol. (Pflüger's)* **181**, 40-4(1920).—The relative amts. of lysis of erythrocytes in mixts. of hypotonic solns. of NaCl and KCl, NaCl and CaCl<sub>2</sub>, KCl and CaCl<sub>2</sub>, and of NaCl, KCl and CaCl<sub>2</sub> showed that for each pair of salts there was an optimal relationship at which the antagonism of ions was maximal and hemolysis was more nearly completely inhibited. With NaCl and KCl this ratio was 1 NaCl:  $\frac{1}{20}$  KCl, or  $\frac{1}{20}$  NaCl: 1KCl. With mixts. of the three salts minimal hemolysis was obtained when the proportions were 1Na:  $\frac{1}{80}$ K:  $\frac{1}{50}$ Ca. G. H. S.

**Hepatic hyperpermeability: a new symptom in diabetes.** JULES HATIEGAN. *Bull. acad. med.* **87**, 236-7(1922).—The elimination of indigo-carmin is associated with the degree of permeability of the liver, and the extent to which the dyestuff is eliminated is of diagnostic value in differentiating the different types of diabetes. Elim-

ination of indigo-carmin in jaundice. *Ibid* 333-35.—Hyperpermeability is not present in diseases of the liver which are associated with jaundice. G. H. S.

**Influence of circulatory disturbances on the gaseous exchange of the blood. I. Oxygen saturation of the arterial blood in tachycardia.** JONATHAN MEAKINS. *Heart* 9, 185-98(1922).—Exptl. tachycardia was produced in dogs and during the expt. the O satn. of the arterial blood was detd. There was no evidence of a decrease in O satn. unless failure of the circulation and pulmonary congestion or edema take place. G. H. S.

**Theory of the colloidal reactions of cerebrospinal fluid.** P. ELLINGER. *Z. physiol. Chem.* 116, 245-65(1921).—E. studied the effect of heating serums of syphilitics and non-syphilitics on the colloidal gold and collargol reactions. The intensity of the latter is diminished with gentle heating and increased by temps. around 80°. Heated serums of non-syphilitics give positive reactions. R. L. SEITZ

**The bacteriophage of D'Herelle.** A. RICHAUD. *J. pharm. chim.* 25, 429-36 (1922).—A discussion of the origin and function of the lytic principle, and its possibilities in producing communal immunity. Cf. *C. A.* 15, 3319. S. WALDBOTT  
APERT: *Vaccins et sérums*. Paris: Ernest Flammarion. Fr. 7.50.

## H—PHARMACOLOGY

ALFRED N. RICHARDS

**The theory of narcosis by anesthetics of the inhalation type.** R. H. MEYER and H. GOTTLIEB-BILLROTH. *Biochim. e terapia sper.* 9, 41-4(1922).—A note of which the exptl. results are to be published in full in *Z. Physiol. Chem.* The anesthetics employed were N<sub>2</sub>O, Me<sub>2</sub>O, CH<sub>2</sub>Cl, (CH<sub>2</sub>)<sub>2</sub>O, EtCl, EtBr, isoamylene, Et<sub>2</sub>O, methylated CHCl<sub>3</sub>, "acetato dimetilico," "formiato dietilico," 1,2-dichloroethylene and CHCl<sub>3</sub>. The mol. concn. of the anesthetics in the lipoids of the brain at the moment of narcosis is calcd. from: percent anesthetic in entering air and coefficient of solubility. It is found to be a const., 0.06, within the limits of exptl. error. H. W. BANKS, 3rd

**Action of ergot on the isolated uterus.** MARIO CIMÒ. *Arch. farm. sper.* 33, 7-16, 31-2, 38-51(1922).—Within physiol. limits a const. relation exists between the action of Ca salts and that of ergot on the isolated uterus of the guinea pig. The more depressing the effect of Ca salts the more the muscular tonus is increased by small doses of ergot, and *vice versa*. Where, in exceptional cases, the virgin uterus fails to react normally to Ca salts, its behavior toward ergot is also anomalous. In such cases ergot can act as a stimulant of muscular contraction only when the tonus is previously lowered. In detg. the activity of an ergot prepn. the uterus should first be treated with a Ca salt in order to establish conditions favorable to the action of ergot and to render less likely a response due to other factors. A. W. DOX

**Pharmacological researches on ichthyol. (Action of ichthyol on metabolism.)** VITTORIO SUSANNA. *Arch. farm. sper.* 33, 52-75(1922).—Oral or subcutaneous administration of ichthyol activates protein metabolism, and increases the elimination of total N, uric acid, S, phosphates and chlorides, as well as the quantity of urine. The elimination of salts proceeds parallel to that of N. The effect is prolonged and the return to normal equil. is gradual. A. W. DOX

**Alcohol in the cephalorachidian fluid. VII. Determination twenty-four hours after the end of the ingestion. VIII. Investigation on the alcohol reaction in patients subjected to the action of chloral and of chloroform.** E. LENOBLE, P. LE GLOAHEC, P. BAUMIER and I. CANN. *Bull. mem. soc. méd. hosp. Paris* 36, 465-70(1920); *Physiol. Abstracts* 6, 128; cf. *C. A.* 14, 3470.—The disappearance of alc. from the cerebrospinal fluid is delayed in heavy drinkers. Only in excessive doses does chloral give rise to traces of alc. in the cerebrospinal fluid; production of formic acid was never observed. CHCl<sub>3</sub>, even in dangerous doses, does not call forth the production of alc. H. G.

**Subacute uranium poisoning of the rabbit.** B. BARTFIELD. *Biochem. Z.* 129, 534-48(1922).—A record of the diet consumed and the amt., d., sugar, albumin, NaCl and total N of urine, and the sugar, NaCl, n, urea and f. p. of rabbits poisoned with U nitrate. Occasional detns. of lactic acid are given when milk sugar was administered intravenously. The excretion of  $I_2$  was also studied after administration of NaI to such animals. The results were not always consistent, although in general they indicate a metabolic disturbance accompanied by an increase in the N of the blood and an undiminished or even increased N excretion by the kidneys. The kidneys are harmed since albuminuria occurs. Glucosuria and hyperglucemia are also produced. B. is of the opinion that the effect of U is not due to radioactivity but to catalytic properties of the element.

F. S. HAMMETT

**Treatment of rheumatism by thorium X. Action on the white blood cells.** CH. AUBERTIN. *Bull. mem. soc. méd. hôp. Paris* 38, 582-8(1922).—A. injected subcutaneously 300 micrograms of Th X into patients with various types of chronic rheumatism. The dose was well tolerated. The results were variable and not particularly favorable. The substance caused a marked diminution in the white cells of the blood, recovery from which occurred after withdrawal.

F. S. HAMMETT

**The cardio-vascular action of pepsin.** M. LOEPER AND A. MOUGEOT. *Bull. mem. soc. méd. hôp. Paris* 38, 721-5(1922).—Pepsin was given in capsules by mouth, injected subcutaneously and intravenously in soln. Oral administration produced no effect. Subcutaneous injections generally yielded a lowering of the blood pressure. Intravenous injections may produce shock.

F. S. HAMMETT

**The action of pepsin on the motility of the large intestine.** M. LOEPER AND J. BAUMANN. *Bull. mem. soc. méd. hôp. Paris* 38, 726-9(1922).—Although pepsin has no effect on the evacuation reflex it does influence intestinal motility in the nature of augmentation.

F. S. HAMMETT

**The action on the organism of saccharin when used as a sweetener for foods.** ED. BONJEAN. *Rev. hyg.* 44, 50-79(1922).—A study of the influence of saccharin solns. on fish life, germination of seeds, acetic and lactic fermentations, enzyme action, and on the dog and man. Below a concn. of  $1/10\%$  saccharin is practically without effect when made up with tablets commercially supplied (60 pts. saccharin, 40 pts.  $\text{NaHCO}_3$ ). Acidity of saccharin alone is likely to affect these processes when in smaller doses. Failure to take into account this acid function is responsible for disagreement in the literature. Saccharin is considered harmless in doses permitted by taste.

JACK J. HENMAN, JR.

**Sensory stimulation by saturated monohydric alcohols.** MARIAN IRWIN. *Am. J. Physiol.* 59, 151-4(1922).—The efficiency of various alcs. on the sensory mechanism of the worm *Allolobophora foetida* ranked as follows:  $\text{Me} < \text{Et} < \text{tertiary Am} < n\text{-Bu} < \text{iso-Am} < n\text{-Am}$ . In anesthetic power the alcs. showed the same order of efficiency. The simpler alcs. show the least physiol. activity and activity decreases with the branching of the carbon chain. Cf. following abstr.

J. F. LYMAN

**Sensory stimulation by unsaturated alcohols, polyhydric alcohols, and chlorohydrins.** MARIAN IRWIN. *Am. J. Physiol.* 60, 270-3(1922).—The behavior of  $\text{C}_4\text{H}_9\text{OH}$ ,  $\text{CH}_2\text{ClCH}_2\text{OH}$ , glycerol monochlorohydrin,  $\text{CH}_2\text{OHCH}_2\text{OH}$ , and  $\text{C}_2\text{H}_5(\text{OH})_2$  toward the sensory cells of the worm *Allolobophora foetida* was studied. The unsatd. alc.  $\text{C}_4\text{H}_9\text{OH}$  shows about the physiol. activity that would be expected on the basis of its chem. activity, being much more active than glycerol or glycol. As regards physiol. activity the more OH groups the less efficient the alcs. are in producing stimulation. A great increase in efficiency results when an OH group is replaced by Cl. This last effect is independent of H-ion concn.

J. F. LYMAN

**Studies on the visceral sensory nervous system. XI. The action of cocaine and**

**aconitine on the pulmonary vagus in the frog and in the turtle.** N. KLEITMAN. *Am. J. Physiol.* 60, 203-18(1922).—The efferent nerve endings of the vagus in the lung and heart of the frog can be paralyzed or greatly depressed by the intravenous injection of cocaine-HCl without paralyzing the vagus center or the efferent endings of the skeletal nerves. Minute doses of aconitine will paralyze the efferent inhibitory endings of the pulmonary vagus in frogs, and larger doses will paralyze the vagus center, resembling the action of cocaine on the same structures. In turtles intravenous injection of aconitine will paralyze the respiratory center, and thus indirectly abolish the spontaneous contraction of the lungs. Aconitine also produces a state of contracture in the turtle's lung. XII. **The response of the isolated esophagus of the frog and the turtle to certain drugs.** Z. BERCOVITZ. *Ibid* 219-33.—The neuromuscular system of the frog esophagus is very sensitive to changes in its O supply. Various drugs (adrenaline, pilocarpine, nicotine, atropine, histamine and pituitrin) have essentially the same action on the two systems of the esophagus, circular and longitudinal. The exact response to the drug is the algebraic sum of the activities of both neuromuscular systems. The drugs used do not affect the isolated esophagus of the frog and turtle alike in all respects.

J. F. LYMAN

**Carbon monoxide asphyxia.** II. **The growth of neuroblast in the presence of carbon monoxide, a demonstration that this gas has no direct toxic action upon nervous tissue.** H. W. HAGGARD. *Am. J. Physiol.* 60, 244-9(1922).—Portions of chick nervous tissue suspended in chickens plasma *in vitro* cultures grew normally in atm. contg. 79% of CO. This indicates that CO has no sp. reaction with nerve tissue but acts in the body only through the asphyxia incident to its combination with hemoglobin. Illuminating gas does inhibit the growth of the chick nerve tissue *in vitro*, indicating the presence of a toxic substance or substances other than CO. J. F. L.

**The action of curare, atropine and nicotine on the invertebrate heart.** A. J. CARLSON. *J. Gen. Physiol.* 4, 559-68(1922).—These alkaloids stimulate and paralyze the central nervous system and peripheral (visceral) ganglia of molluscs and arthropods, but do not paralyze the motor nerve endings of skeletal or visceral muscle. Other effects are: stimulation and paralysis of the denervated heart, paralysis or block of the cardioinhibitory nerves, but not of the cardioaccelerator nerves. These alkaloids act primarily on the heart ganglion of *Limulus* but not on the heart muscle or intrinsic motor nerve fibers. 22 genera of molluscs and 3 of arthropods were used in this study.

CHAS. H. RICHARDSON

**Effect of pharmacologic agents on the peripheral vascular apparatus.** WALTER ЯАCOB. *Arch. exp. Path. Pharm.* 86, 49-78(1920); cf. *C. A.* 16, 293.—The observations were made upon the vessels of the web of curarized frogs, where it is possible to observe the localized effects of various poisons on the arterioles and capillaries. Veronal causes a persistent maximal local dilatation. Cocaine causes vasoconstriction and vessels so constricted may be dilated by veronal. Adrenaline in 1:500,000 will cause constriction of vessels dilated by veronal, whereas with normal vessels it requires a concn. of about 1:1000 to be effective.

G. H. S.

**Fixation and neutralization of poisons in the nervous centers.** JEAN CAMUS. *Bull. acad. med.* 86, 302-5(1921).—Various poisonous substances were injected into the spinal canal. Certain of them, as PbCl<sub>2</sub>, act only after an incubation period; although most mineral chlorides and sulfates act immediately. The state of the meninges in some measure detcs. the degree of fixation of the chemical. With an aseptic meningitis, Pb when injected intravenously is toxic. Attempts at neutralizing the action of Pb by converting it into an insol. compd. were not entirely successful, since the resulting substance induces secondary reactions of toxicity.

G. H. S.

**Influence of calcium and potassium ions on toxic actions on the heart.** I. S.

G. ZONDEK. *Arch. expl. Path. Pharm.* **87**, 342-55(1920); cf. *C. A.* **15**, 707.—The effect of Ca and K ions upon the action of chloral hydrate and muscarine on the frog heart was detd. With a heart in diastolic arrest due to chloral hydrate the addition of Ca ions restores activity. Chloral hydrate and K ions show similar toxicologic properties; both lead to a reversible diastolic relaxation of the heart muscle, and against both the Ca ion is antagonistic. The effects of muscarine also are largely inhibited by the presence of the Ca ion, while K is in no way inhibitory.

G. H. S.

**Choline as the hormone of intestinal action. III. Relation of choline to the activity of organic acids in the intestines.** J. W. LE HEUX. *Arch. ges. Physiol.* (Pflüger's) **190**, 280-300(1921).—The effect of choline and of its compds. with org. acids was detd. upon the isolated intestine prepn. The esters were more effective in inducing contraction than was choline itself, although among themselves they showed a wide variation. Thus as compared with choline (= 1), the acetic ester = 1000, the propionic = 300, the formic = 100, the *n*-butyric = 40, isovaleric = 15, benzoic = 2, and succinic = 1. If the tissue is freed of choline by washing, the addition of the Na salts of the acids is without effect. In some cases an activation results from the subsequent addition of choline. With the esters as with choline atropine is antagonistic. The influence of choline upon intestinal action may be associated with the combination of the choline there present with the org. acids through the intervention of a synthetic enzyme. **IV. Effect of choline on normal gastrointestinal activity.** *Ibid.* 301-10.—By means of the X-ray the effect of the administration of choline to cats was detd. Intravenous injections of 4 to 10 mg. of choline-HCl were well tolerated and caused increased activity of both stomach and intestine. **V. Therapy of gastrointestinal stasis after chloroform narcosis.** MALTE VON KÜHLWEIN. *Ibid.* **191**, 99-107(1921).—Cats kept under  $\text{CHCl}_3$  narcosis for 2 hrs. and examd. by X-ray showed a stasis of the gastrointestinal tract comparable to that observed in man after the administration of narcotics. The complete stasis persisted for 2 hrs. and had not completely disappeared after 20 hrs. To such animals choline-HCl given intravenously in amts. varying from 0.005 to 0.015 g. per kg. caused a marked effect upon the stasis. No harmful effects could be detected. There is no evidence that an actual choline reduction occurs in the body during  $\text{CHCl}_3$  narcosis.

G. H. S.

**Archiv für experimentelle Pathologie und Pharmakologie.** Edited by R. Boehm. Leipzig: F. C. W. Vogel. M 40.

**Formulaire Astier 1922 (Thérapeutique et Pharmacologie).** 2nd Ed. Paris: Vigot frères, 23 rue de l'École-de-Médecine. 25 fr. Reviewed in *Reperl. pharm.* **78**, 60(1922); *Chem. Weekblad* **19**, 57(1922).

GILG, ERNST and BRANDT, WILHELM: **Lehrbuch der Pharmakognosie.** 3rd Ed. revized. Berlin: Julius Springer. 423 pp. M 70, bound.

## I—ZOÖLOGY

R. A. GORTNER

**The enzymes of the digestive organs of scorpions.** E. SARIN. *Biochem. Z.* **129**, 359-66(1922).—Catalase, amylase, lipase, pepsin, trypsin and chymosin were found present in the liver of scorpions. No enzymes were found in the mid-gut either in the *pars lecta* or the *pars meda*. The paunch salivary glands contained lipase, pepsin, trypsin and chymosin. Inulase and invertase were not detected in any of the portions examd.

F. S. HAMMETT

**The pigment and wax of the aphid (*Schizoneura lanigera*).** FR. N. SCHULZ. *Biochem. Z.* **127**, 112-9(1922).—The red pigment from the wooly apple aphid is intense red-violet in alc.; with addition of alkali intense violet, while a trace of acid changes it to yellow. Spectroscopically, it resembles cochineal pigment with some differences. On dig. the alc. soln. a jelly-like red mass seps. in which fat-like drops appear.  $\text{Et}_2\text{O}$

dissolves the fat-like mass, but the pigment is insol. From the  $\text{Et}_2\text{O}$  soln. the pigment is no longer sol. in hot or cold alc., but is sol. in  $\text{H}_2\text{O}$  giving a bright red soln. Extn. of the alc. exhausted aphids with  $\text{Et}_2\text{O}$  gave a yellow-brown soln. contg. on diln. a fatty mass which gave some crystals in cold alc. This pigment appears to be related to the lipochrome pigments. The wax mass is difficultly sol. in cold but easily sol. in hot alc. from which it largely seps. in crystals on cooling leaving the "lipochrome" in soln. The white recrystd. wax m.  $48-9^\circ$  and is sol. in  $\text{Et}_2\text{O}$ ,  $\text{CHCl}_3$ ,  $\text{C}_6\text{H}_6$ , hot alc. and concd.  $\text{H}_2\text{SO}_4$ . It is not a true wax, but a glyceride of a satd. fatty acid. Glycerol content 7-10%; yield of fatty acid 76%. The fatty acid m.  $36^\circ$  and has a mol. wt. of 327, corresponding to a 20-22 C-atom acid, which cannot be identified with the known normal fatty acids. This fat bears no close chem. relation to bee, cochineal or psylla wax.

CHAS. H. RICHARDSON

**Kinetics of the bioluminescent reaction in Cypridina.** I. W. R. AMBERSON. *J. Gen. Physiol.* 4, 517-34(1922).—Studies were made of the time relations in this reaction and specifically the rate of decay of the light produced when aq. solns. of enzyme and substrate are mixd. together. A photographic method was devised and is described in detail. II. *Ibid.* 535-8.—The decay curve for the luminescent reaction in *Cypridina* agrees completely with the theoretical expectation of a monomol. reaction if it is assumed that the light intensity at any instant is proportional to the reaction velocity at that instant. The exptl. values satisfy the equation,  $\log I = -kt + \log Ak$ , where  $I$  = light intensity,  $t$ , time,  $A$ , the initial concn. of a single reactant and  $k$ , a const. During the first sec. or 2 of the reaction, a brilliant flash of light occurs the value of which is proportionally higher than the immediately surrounding values. It is probably indicative of a heterogeneous system and due to the fact that the surfaces of the org. catalyst are clean at the beginning of the reaction, permitting a rapid adsorption of the substrate. Stirring the solns. was without effect on the reaction velocity or the form of the decay curve. At the concns. used, the reaction velocity was proportional to the enzyme (luciferase) concn. With other factors const., changes in substrate concn. did not affect the value of  $k$ . A reduction in luciferin concn. results only in a decrease in the value of  $Ak$ . The temp. coeff.  $(Q_{10})$  was high: 4.5 for the  $15-25^\circ$  interval, 3.0 for the  $25-35^\circ$  interval.

CHAS. H. RICHARDSON

**The effect of temperature on the phototropic response of Necturus.** W. H. COLE. *J. Gen. Physiol.* 4, 569-72(1922).—*N. maculosus* is negatively phototropic. The reaction time changes little with light intensities of 1,875-8,000 candle meters, indicating that the max. amt. of chem. stimulation was produced in a very short time with the lowest light intensity used. Reaction time varied inversely with the temp. between  $2^\circ$  and  $32^\circ$ . The decrease in reaction time with increased temp. is due to the increase in the velocity of the chem. processes which cause muscular movement and not to any effect upon the photochem. reaction. The reaction time of cycless animals was almost identical with that of normal animals, showing that the skin is the most important receptor of the photic stimulus.

CHAS. H. RICHARDSON

**Effect of supranine on the growth of tadpoles.** FRIEDRICH BILSKI. *Arch. ges. Physiol. (Pflüger's)* 191, 108-27(1921).—Supranine in very small amts. stimulated growth. The soln. was active even though it had undergone a partial oxidation.

G. H. S.

## 12—FOODS

W. D. BIGELOW AND A. E. STEVENSON

**Nutrition questions from the standpoint of science, the household and legislation.** A. JUCKENACK. *Z. Nahr. Genussm.* 43, 9-24(1922).—General discussion is followed by new legislative proposals.

D. B. DILL

**The refractometer and the interferometer.** PAUL HIRSCH. *Z. Nahr. Genussm.* **43**, 65-78(1922).—The application of these instruments to problems in food and biological chemistry is described. D. B. DILL

**Infants' food flours.** FRANZ HAMBURGER. *Wiener klin. Wochschr.* **34**, 36-7 (1921).—A review and criticism of the use of com. infants' food in Austria at present. W. A. PERLZWEIG

**Analytical researches on the aging of condensed milk.** G. VIALE AND A. RABENO. *Biochim. e terapia sper.* **8**, 324-52(1921).—An extensive and complete study of the changes occurring in condensed milk on aging. Analyses were conducted in the summer of 1920 upon samples packed in Dec. 1919, Sept. 1919, July 1919, Dec. 1918, Oct. 1917, June 1912. The following detns. were made on each sample and the results expressed in tabular form: sp. gr.,  $H_2O$  content and dry residue, viscosity, cond., total acidity, enzymes (oxidizing and reducing), time of coagulation of the casein, total N, casein N, albumin N, non-protein N, amino N, polypeptides,  $NH_3$ , carbohydrates, fats and lipoids, general appearances, color, etc. For tabulated exptl. results the original must be consulted. General conclusions: The most noticeable alterations observed are those of general appearance (color, etc.), viscosity, and chem. constituents. The last affect principally the N substances, the fats and the carbohydrates. Enzymes are inactivated by the methods of condensation and preservation of the milk, while amino acids become degraded to more simple substances. A gradual hydrolysis of proteins occurs with formation of polypeptides and finally amino acids and  $NH_3$ . Lactose and sucrose also are hydrolyzed to monosaccharides. The neutral fats are saponified and volatile fatty acids are decomposed. These transformations are slight during the first months and become greater during several years of storage. The brown color in older samples is probably due to the oxidation of amino acids (tyrosine) with formation of melanins, and modification of the lactose. Very old samples become less sweet as they are lacking in sugars, especially sucrose. A bibliography of 43 references is given. H. W. BANKS, 3RD

**The degree of sweetness of sweet substances.** THEODOR PAUL. *Z. Nahr. Genussm.* **43**, 137-49(1922).—The degree of sweetness of saccharin and dulcin is not a const. It decreased with the increasing concn. of the soln. Thus the value for saccharin may vary from 200 to 700 and for dulcin from 70 to 350. A no. of experts were unable to differentiate by the taste between solns. of sugar and artificial sweetener. In mixts. of sweeteners the total degree of sweetening is approx. equal to the sum of the degrees of sweetening of the constituents. Cf. *C. A.* **15**, 1361; <sup>\*</sup>**16**, 973.

D. B. DILL

**Methods for the examination of artificial honey, especially the determination of sucrose and starch sirup.** A. BEHRE. *Z. Nahr. Genussm.* **43**, 24-44(1922).—Total solids can be detd. refractometrically with good results. Starch sirup can be detd. by polarization or by the I method. During inversion with mineral acid the glucose is unchanged but fructose is partially decomposed to  $HCOOH$  and possibly  $H_2CO_3$ . There also result condensation products of fructose similar to levulose which possess lower reductive powers and less optical rotation. On this account the detn. of sucrose by the Clerget-Fehling or by the polarization method is inaccurate and the use of the I method (oxidation with excess I in weakly alk. soln.) is advocated. D. B. DILL

**A study of methods of minimizing shrinkage in shell eggs during storage.** L. H. ALMY, H. I. MACOMBER AND J. S. HEPBURN. *J. Ind. Eng. Chem.* **14**, 525-7(1922).—Immersion of eggs for short periods in heated or unheated  $H_2O$  solns. of mineral or org. acids, mineral salts, or soap were of but slight value in reducing shrinkage in eggs held at room or higher temp. The loss in wt. of eggs treated with heated cottonseed oil was 6.3% and of those treated with a heated mineral oil (sp. gr. 0.899, flash point  $365^\circ F.$ , viscosity at  $100^\circ F.$  134 units, Saybolt) was 7.4% of that of untreated eggs.

Lighter mineral oils, two other vegetable oils, and an animal oil was less satisfactory. Addition of gums, waxes, or rosin failed to increase the efficiency of the better mineral oil. 1 or 2% of soap markedly increased the sealing value of the more inferior mineral oils.

L. H. ALMY

**Iron analysis of kale and turnip greens.** MARIETTA EICHELBERGER AND MAUDE ASBURY. *J. Home Econ.* 14, 131-2(1922).—The Fe contents of kale, turnip greens, and spinach, resp., were, 0.00312, 0.00269, and 0.00272%.

HELEN N. ELLIOTT

**The banana.** L. PYNAERT. *Bull. agr. Congo Belge* 12, 530-66(1921).—The results are given of an extensive study of the chem. compn. of bananas. In many cases the org. compds. present as well as ultimate analyses are shown. Numerous analyses of different parts of the fruit are reported and compared with analyses of fruit grown in different places and in different stages of maturity. Dried banana flour is an easily digestible food showing an av. compn. as follows: H<sub>2</sub>O 13.7%, ash 2.6%, org. matter 83.7%.

M. S. ANDERSON

**Some changes in the composition of California avocados during growth.** C. G. CHURCH AND E. M. CHACE. U. S. Dept. Agr., Bur. of Plant Ind., *Bull.* 1073, 1-22 (1922).—No satisfactory correlations between phys. properties and maturity have been found in the avocados examd. The proportion of many of the constituents of the avocado changes during its development, the most marked change being the increase of the fat content. This takes place rapidly while the fruit is immature and much more slowly as it approaches maturity, with possibly a slight decrease if the fruit remains too long upon the tree. It is accompanied by a decrease in sugar content. Fruits rich in fat (above 20%) contain at least 70% of that constituent on a water-free basis at maturity. On storage of immature fruits there is an apparent increase in the proportion of fat, accompanied by a decrease in the sugar content and undetd. matter. Mature fruits on storage do not show this increase to the same extent and at times show some loss.

W. H. ROSS

**Note on operations at Elaesis in Barumbu.** L. THON. *Bull. agr. Congo Belge* 12, 522-9(1921).—A chem. study is reported of the various products of the palm tree showing the compn. of hulls, shells and pressed cake. Analyses show a very significant fertilizing value in the waste products. The production of palm oil is a growing industry in the Belgian Congo.

M. S. ANDERSON

**Relation of initial temperature to pressure, vacuum and temperature changes in the container during canning operations.** C. A. MAGOON AND C. W. CULPEPPER. Dept. Agr., Bur. Plant Ind., *Bull.* 1022, 1-52(1922); cf. *C. A.* 15, 3531.—In tin cans contg. various quantities of water changes of pressure vary somewhat from the calcd. values, owing to the distortion of the can under the changed conditions. With food materials in which a free liquid fills the interspaces the rate of change of pressure and of temp. is very rapid, but with material of heavy consistency the rate of change of temp. at the center of the can is very slow. In either case the pressure does not reach a max. at the time of max. temp. but continues to rise during the processing period because of the decompn. of the food material with consequent liberation of gases. In the heat exhausting of cans the vacuum may not be proportional to the av. temp. of the material at the time of sealing but is detd. largely by the temp. of the head space. The vacuum developed in tin cans is generally below the theoretical, the causes contributing to the variation from theoretical values being the distortion of the can, the swelling of colloidal substances and the liberation of gases during processing. For most vegetables the optimum temp. for the sealing of No. 2 cans is 80° to 85°, and for No. 3 cans 75° to 80°.

W. H. ROSS

**Polygala butter.** *Rev. gén. froid Aug. 1921; Industrie chimique* 9, 213(1922).—



*Polygala butyracea*, which grows in Indo-China, contains 30% of a fat consisting almost entirely of palmitin. When fresh it could be used to advantage in the margarin industry.

A. P.-C.

**Inspection of lard.** A. BÖMER. *Z. Nahr. Genussm.* **43**, 87-99(1922); cf. *C. A.* **15**, 3156.—Methods are reviewed for the detection of adulteration of lard. Reliance is placed on the const.  $Sg + 2d$  for the detection of added hardened lard.  $Sg$  represents the m. p. of the glycerides and  $d$  the difference between the m. p. of the glycerides and of the fatty acids. For pure lard, this value may vary from 74.3 to 76.6. For hardened lard it usually lies between 65 and 70.

D. B. DILL

**The value of whale meat as human food.** AGNES F. MORGAN AND EDITH L. BROWN. *J. Home Econ.* **14**, 267-70(1922).—Proximate analyses of whale flesh and  $H_2O$  exts. of the same indicate that the digestibility of whale protein is similar to beef protein and is in a high degree available for tissue repair in the human organism. An analysis of freshly thawed whale flesh gave  $H_2O$  56.9, ash 0.38, protein 25.3, fat 17.4, undetd. 0.02%. The cold  $H_2O$  ext. gave total N 3.43, N insol. in cold  $H_2O$  2.50, coagulable N 0.35, meat bases 0.58%.

L. D. ELLIOTT

**Caviar and derived preparations.** P. BUTTENBERG. *Z. Nahr. Genussm.* **43**, 79-85(1922).—The varieties of caviar on the German market are discussed. Types of adulteration are described.

D. B. DILL

**The manufacture of vinegar with rotary acetifiers.** P. HASSAK. *Deut. Essigindustr.* **25**, 149-52, 157-8(1921); *Chimie et industrie* **7**, 985(1922).—H. concludes from com. scale expts. that rotary acetifiers give satisfactory results from every point of view especially for the production of wine vinegar, and in general for all vinegars rich in flavor. They offer no advantages for the manuf. of malt or cider vinegars.

A. P.-C.

**The factors affecting temperature in rapid acetification.** H. WÜSTENFELD. *Deut. Essigindustr.* **25**, 237-9, 245-6(1921); *Chimie et industrie* **7**, 985(1922).—As a result of observations carried out by W. on the rapid acetification app. at the Berlin expt. station, he concludes as follows. The temp. depends primarily on the physiol. condition of the "tree," i. e., on the number of active cells, their condition and species. It also depends on the amt. of alc. passing daily over the cells, and on the quantities of alc. and of acid retained by the shavings. Working with concd. solns. lowers the temp., and working with dil. solns. raises it; so that by adjusting the alc. content of the liquor to be acetified the temp. can be regulated. Oxidation takes place especially in the upper portions of the "tree," where there is plenty of alc. and the temp. is highest, and it gradually decreases lower down; but when there is excess of alc. the temp. falls appreciably. The temp. is, to a certain extent, regulated automatically: If the atm. temp. rises, the temp. of the warmer parts of the mass will rise above the optimum, causing a slowing down of the acetification and corresponding drop in the temp. If the atm. temp. falls, the converse takes place. As the temp. is highest where acetification is most active, the activity of each layer of shavings can be obtained by taking the temp.

A. P.-C.

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The employment of pure cultures of microorganisms in industry (RAHN) **16**.

LALAUURIE, G.: *Contribution a l'etude des ferments du lait*. Toulouse: Libr. Marquette. 79 pp. Fr. 4.50.

RICHMOND, HENRY DROOP: *Dairy Chemistry*. Philadelphia: J. B. Lippincott Co. 490 pp. \$6.

## 13—GENERAL INDUSTRIAL CHEMISTRY

HARLAN S. MINER

**Crushing, storing and pulverizing.** L. H. STURTEVANT. *Rock Products* **25**, No. 3, 28-9(1922).—Almost entirely mechanical. The following topics are discussed: phosphate rock, unloading power shovels, crushing, pulverizing, air separators, dust collectors, storage, and labor requirements.

E. F. PERKINS

**The efficiency and capacity of fractionating columns.** W. A. PETERS, JR. *J. Ind. Eng. Chem.* **14**, 476-9(1922).—Using W. K. Lewis' formula for measuring the efficiency of fractionating columns, P. investigated (1) sieve plate, (2) bubbler cap plate and (3) filled columns. The efficiency of types (1) and (2) was the same for a given sepn. The efficiency of columns packed with iron rings varied inversely as the size of the rings. The efficiency of any column depended on the materials being sepd. A method was developed for figuring the comparative cost of columns for a given sepn., and the capacity of the columns detd.

E. G. R. ARDAGH

**The plate efficiency of a continuous alcohol still.** C. S. ROBINSON. *J. Ind. Eng. Chem.* **14**, 480-1(1922).—W. K. Lewis' formulas (see preceding abstr.) require (1) the relation between the liquid and vapor compns., and (2) the plate efficiency. R. has made 3 runs, under not widely varying conditions, with alc.-water mixts., in a still of the modern Barbet type fitted with plates and caps as described by Barbet and Mariller. The results for the plate efficiency varied widely, being 40, 24 and 56%.

E. G. R. ARDAGH

**The simple distillation of hydrocarbon mixtures.** W. K. LEWIS AND C. S. ROBINSON. *J. Ind. Eng. Chem.* **14**, 481-4(1922).—Basing their calcs. on Rayleigh's equation for simple distn., L. and R. illustrate a method by which one can plot the Engler distn. curve for a mixt. of 2 components.

E. G. R. ARDAGH

**The efficiency and design of rectifying columns for binary mixtures.** W. K. LEWIS. *J. Ind. Eng. Chem.* **14**, 492-7(1922).—"Basic equations of general applicability have been derived by means of which it is possible to calc. the theoretical rate of rectification within any column for the terminal conditions and the amt. of overflow, and compare this rate with that actually realized. The results of these calcs. agree satisfactorily with actual tests. A complete example has been computed showing the use of these equations in the design of a continuous column, the design of min. overflow, of the best practical overflow, of the number of plates required and of the point of introduction of the feed." Quant. discussion is limited to alc.-water mixts.

E. G. R. ARDAGH

**Recent developments in power production.** D. L. SELBY-BIGGE. *J. Iron Steel Inst.* (London), adv. proof, 1922, 40 pp.; *Iron & Coal Trades Rev.* **104**, 659-61(1922).—Because of high standards attained in the engine room and power plant only trifling economies can be looked for in these places, but in boiler houses savings are possible. The chief sources of cheap power are coal at the collieries and waste gases at iron and steel plants. Much refuse coal, often high in ash, is now recovered by froth flotation processes, 98% and more of the heating value being saved, at a cost of 4 d. per ton. Capacity of boilers and pressures at which they are used have greatly increased in recent years. Superheaters fitted integrally to boilers give steam at 650-750° F., a value not likely to be exceeded because of the properties of steel at these temps. Mechanical stokers, with either natural or forced draft, offer unquestioned advantages over hand firing; the underfeed and multiple retort types are the most promising. Blast furnace gases (uncleaned) for firing boilers are used with an external chamber to prevent clogging of the boilers with dust, and do not give as good an intermixture of air and gas as a Bunsen type burner. With clean gas the latter type is used, and efficiencies are raised

from 65 to 75%, or for each pound of steam there would be required 16 cu. ft. of 100 B. t. u. gas. From coke ovens 80% of the gas will be available in the form of waste heat, at a temp. of 1800 to 2000° F., and 20% in the form of surplus live gas of 450 to 500 B. t. u. The evaporation obtainable from the combination of waste heat and live gas is equal to about 1.25 tons of water (at 212° F.) per ton of coal carbonized. Gases from reheating, puddling and other furnaces can evaporate 5.5-6 lbs. of water per lb. of coal burned on the furnace, if the gases are delivered at 1800° to 2000° F. Gases from regenerative furnaces, at 1000° to 1150° F., used with boilers provided with economizers and induced draft fan, evaporate from 2.27 lbs. of water, with gas at 900° F., to 3.26 lbs., with gas at 1100° F., per lb. of coal burned on the producer, or 2000 to 2200 lbs. of water per ton of steel made (gas entering at 1100° F.). With waste-heat boilers (Kirke), tube efficiencies of 90% are claimed. Pulverized fuel is increasing in use. Data are given. A typical American installation gives efficiencies of 86.3-89.1%, the latter on coal of 11491 B. t. u. In European plants working on inferior (high-ash) coals efficiencies of 75 to 81% were obtained. Of the "Central" and "Unit" types of powdered coal equipment the latter is preferred. Powdered coal, even high in ash and moisture, is used very efficiently in firing metallurgical furnaces. Steam turbine practice has been marked during the last ten yrs. by the development of the use of high-pressure steam and high superheat, and by the adoption of higher turbine speeds. Turbo compressors, built in units of 30,000 cu. ft. of air per min. at 100 lbs. pressure, and turbo blowers giving 35,000 cu. ft. of air per min. at 40 lbs. per sq. in., have the same advantages over the reciprocator that the steam turbine does over the steam engine. Recent improvements in centrifugal pumps for water circulation have assisted in the economical operation of high vacua condensers. Surface condensers give a condensate that can be used again as a boiler supply, an advantage where suitable feed water is not available, but they are high in first cost and maintenance. Jet and ejector condensers have had their usefulness extended through the introduction of modern water treatment processes for boiler feeds. Gas engine installations of 15,000 to 20,000 h. p., working on blast furnace gases, are now operating in Great Britain. Oil engines, especially of the Diesel type, show costs ranging around 0.75 to 0.81 d. per kw. hr. Water power is a negligible factor in Great Britain. Coal remains the basic source of power, and therefore attention is directed towards (1) cleaning of fuel prior to combustion, (2) reduction of labor and economical combustion of fuel by (a) efficient mechanical stokers and (b) use of powdered coal, (3) purification, softening and heating of boiler water, and provision for an efficient cooling plant for condensing purposes, (4) closer and more scientific control of the boiler house, (5) a more comprehensive utilization of waste gases from furnaces, and (6) the development of markets to absorb surplus power available from collieries, iron and steel works. Abundant illustrations, test data and descriptions of plants are given.

W. C. EBAUGH

**The plant manager and the chemist.** GEO. L. O'BRIEN. *J. Ind. Eng. Chem.* **14**, 650-1 (1922). E. J. C.

**Can the college do anything for industry?** EDWARD ELLERY. *J. Ind. Eng. Chem.* **14**, 544 (1922).—The college can reduce the period of unproductiveness of their graduates when they enter industry by training them in the acquisition, recognition, application and description of facts, and finally in handling an original problem. For this purpose it is essential that there be (1) small instructional groups, (2) superior students separated from inferior students, (3) strongest teachers in charge of freshmen and seniors, and (4) a limitation of the number of students and of the number of hours the good teachers teach.

W. C. EBAUGH

**Public recognition of the honor of invention.** ALEXANDER LANG. *Chem.-Ztg.* **46**, 428 (1922).—The (German) patent office recently published a notice that hereafter

the name of the inventor, and not merely that of the applicant, must be given in an application for a patent. Although theoretically a patent is a right to immaterial property, and is not concerned with the rights of persons, nevertheless the public good is served best if recognition is given to inventors.

W. C. RHAUGH

**Present day depreciation practice.** E. KESSLER. *Chem.-Ztg.* 45, 1239(1921); 46, 380-2(1922).—A discussion of accounting methods, especially with respect to the present uncertain (German) currency standards.

W. C. RHAUGH

**Electric insulation materials, especially bakelite.** A. BULTEMAN. *Kunststoffe* 12, 66-8, 76-8, 82-4(1922).—General discussion of the use of bakelite as a raw material for the manuf. of insulating material.

C. J. WEST

**Early references pertaining to chemical warfare.** C. A. BROWNE. *J. Ind. Eng. Chem.* 14, 646(1922).

R. J. C.

**Chemische Technologie der Heiz- und Leuchtstoffe des Erdöls, der Fette, der Schiess-, Spreng- und Zündmittel.** Edited by H. F. Baumhauer and Bernhard Neumann. Braunschweig: F. Vieweg und Sohn.

HASSACK, KARL: *Warenkunde*. Berlin und Leipzig: Vereinigung wissenschaftl. Verleger. 141 pp.

KORPAL, JOS.: "Chemia." *Rezepte- u. Fabrikationsverfahren d. chem.-techn. Industrie*. 2nd Ed. revized. Mähr.-Ostrau: J. Kittl. 83 pp. Kart. Kc. 27.50.

KUHN, MÜLLER, HOTTINGER: *Materiallehre für Lehrlinge, Arbeiter, Betriebsangestellte der Metallindustrie und für den Unterricht in Werk- und Gewerbeschulen*. Frauerfeld: Huber & Co. 288 pp. Fr. 7.50. Reviewed in *Schwiz. Chem.-Ztg.* 1922, No. 17, Suppl. p. I.

**Separating extractive substances from volatile liquids.** H. BOLLMANN. U. S. 1,417,477, May 23. Mixed aq. org. liquids such as alc. or  $C_4H_{10}$  with  $H_2O$  and extractive substances are distd. and 2 fractions are collected contg. at least part of the  $H_2O$  and volatile substances. An additional distillate is formed from the residue and mixed with the lighter of the previously collected fractions.

## 14—WATER, SEWAGE AND SANITATION

EDWARD BARTOW

**Report on water.** J. W. SALE. *J. Assoc. Agr. Chem.* 5, 379-88(1922); cf. C. A. 16, 453.—The Weselzsky method for the detn. of I and Br in waters was studied. The method depends upon the selective oxidation of Br in acid soln. by  $Cl$  water, Br being set free, sepd. from the I by distn. in a stream of  $CO_2$  and absorbed in a bulb contg. a soln. of  $KOH$ . The I converted into iodic acid in the reaction flask is titrated with standard thiosulfate after the addition of  $KI$ . The Br converted into bromate in the adsorption bulb and freed from chlorate by boiling to dryness is likewise titrated with thiosulfate. Data showed that the method was not satisfactory for Br but gave good results for I provided 5 cc. I to 1  $HCl$  are used in the reaction flask and it is proposed to make this a tentative method for the detn. of I in the presence of  $Cl$  and Br. Methods for detg. small quantities of Pb, Cu and Zn will be studied next year. The proposed procedure consists in eliminating the coloring matter by pptg. the metals with  $(NH_4)_2S$ . The Pb is sepd. as  $PbSO_4$  and detd. colorimetrically as  $PbS$ . The Cu is sepd. as  $CuS$  and detd. colorimetrically with  $K_4Fe(CN)_6$ . In the filtrate from the Cu, the Fe is held in soln. with citric acid. The Zn is pptd. as  $ZnS$  and detd. turbimetrically with  $K_4Fe(CN)_6$ . Tentative methods are given for detg. moisture and insol. material in

salt. It is recommended that analyses be reported in terms of mg. per l. or in case of highly coned. waters in g. per l.; in case of medicinal waters grains per quart. Directions for making hypothetical combinations are given together with combining wt. values and their reciprocals.

G. C. BAKER

**The frequent impurity of distilled water.** A. RICHAUD. *J. pharm. chim.* **25**, 469-77(1922).—A summary of the sources of impurities in distd. water, and methods of testing with a specified set of reagents are given.

S. WALDBOTT

**The determination of hardness in water.** A. C. RÖTTINGER. *Z. Ver. Gas-Wasserfach. in Österreich u. Ungarn* **59**, 13-22, 36-9; *Wasser u. Abwasser* **15**, 205-6 (1921).—R. recommends titration with 0.02 N HCl for carbonate hardness and titration with K palmitate for total hardness, with a suitable correction for the end-point. Results are considered as only approx.

F. W. M.

**The permissible salt concentration in drinking water.** H. STOFF. *Gas u. Wasserfach* **65**, 50(1922).—S. contends the allowable salt concn. of wastes entering the Elbe and Weser rivers should not be raised from 250 to 350 mg./l., and that the salt and potash plants should be required to purify at least part of their wastes before allowing them to enter these rivers. He supports his views by references from various authors.

MARTIN E. FLENTJE

**The gas content of the water of Lake Himmelsdorfer near Lübeck.** BRUNO SCHULZ. *Naturwissenschaften* **10**, 307-8(1922).—The deeper H<sub>2</sub>O of the Himmelsdorfer Lake contains 300 mg. per l. of H<sub>2</sub>S, the highest content of any natural H<sub>2</sub>O known. Complete data and information on this lake have now been published (cf. W. Halbfass, *Der Himmelsdorfer See bei Lübeck*, *Mitt. Geograph. Ges. Naturhistorischen Museums Lübeck* **2**, No. 24(1910); R. Griesel, *Physikalische und chemische Eigenschaften des Himmelsdorfer See bei Lübeck*, *Ibid* **2**, No. 28(1921); *Dissertation*, Ros-tock).

C. C. DAVIS

**Water supply of Upper Silesia and its future.** D. HACHE. *Gas u. Wasserfach* **65**, 49-51, 67-71(1922).—H. gives a detailed description and enumeration of the existing waterworks plants in Upper Silesia, with capacity, location and equipment of each. He also discusses plans for the necessary future supply.

MARTIN E. FLENTJE

**Industrial wastes in relation to water supplies.** WELLINGTON DONALDSON. *Am. J. Pub. Health* **12**, 420-1(1922); *Pub. Health Eng. Absts.* July 1, 1922; cf. *C. A.* **15**, 1367.—Three classes of wastes interfere with the operation of water purification plants. The first includes those of an oily, fibrous or pulpy nature which cake or coat the filter sand and cause trouble from washing beds. The second includes those having chem. or phys. properties that act as protective colloids and interfere with the normal reaction of alum and FeSO<sub>4</sub> in coagulation. In the third class are placed all wastes which combine with Cl and either destroy its sterilizing action or cause objectionable tastes and odors from new compds. formed. Tannery wastes and dye liquors belong to the second class and those from gas-houses, by-product coke works and producer plants are mentioned under class three.

G. C. BAKER

**The movements of silt in streams.** H. KREY. *Zentr. Bauverwältg.* **39**, 212-14, 217-20; *Wasser u. Abwasser* **15**, 215-6(1921).—By numerous current-meter studies K. developed differential equations to express the horizontal and vertical velocities in flowing streams. The effect of these currents on turbulence and turbidity is discussed

F. W. M.

**Action of open and closed filters in iron removal.** KARL KISSKALT. *Gas u. Wasserfach* **65**, 85-6(1922).—The expts. were to det. whether open or closed filters were desirable after the coke Riessler in Fe removal plants. An open slow sand filter with 1 sq. m. surface area, and a closed filter with 6 sq. m. surface area and a capacity of

50 cu. m. were used in connection with a Riessler of 33 sq. m. surface area and a capacity of 100 cu. m. per hr. With a water contg. from 2.4 p. p. m. Fe, it was found that the slow sand filter did not entirely remove the Fe from 1 cu. m. of water, while the closed filter completely removed the Fe from 50 cu. m. of the water. MARTIN E. FLENTJE

**A study of the efficiency of a Riessler in iron removal.** KARL KISSKALT. *Gas u. Wasserfach* 65, 37-9(1922).—The efficiency of a Riessler was studied by using gelatin as a protective colloid in an Fe-bearing water, thus preventing the coagulation of colloidal Fe on passing through the tower. The results showed that the amt. of uncoagulated Fe leaving the Riessler is not dependent on the amt. of Fe in the raw water, but rather on the amt. of Fe removed in the tower. This then throws the burden of the Fe removal on the filters, in case the coke tower fails at any time to remove the dissolved Fe, and in that process also fails to coagulate the Fe in suspension. M. E. F.

**New experiences in the cleaning of pipes from obstructing roots and incrustations.** SCHULZE. *Gesundh. Ing.* 45, 285-6(1922).—S. describes the Remert machine for removing roots and incrustations from pipes. It consists of toothed wheels, resembling circular saws, which when drawn over the obstruction remove them quickly and completely. The machine has been successfully used in removing hard  $\text{CaCO}_3$  scale and tar from gas pipes. MARTIN E. FLENTJE

**Filter sand.** G. ANKLAM. *Tonind.-Ztg.* 43, 655; *Wasser u. Abwasser* 15, 61 (1921).—The av. size of sand grains should be 0.4 to 0.5 mm. for filtration of ground water. For deferrization the size should be larger, about 1.0 mm. F. W. M.

**Sewage disposal by fine screens at Bridgeport, Conn.** ANON. *Am. City* 26, 245(1922); *Pub. Health Eng. Absts.* July 1, 1922.—Reinsch-Wurl screens prepare the sewage for disposal by dlm. Three screens are designed to handle 35 mil. gal. per day preceding pumping. Only 2 screens have been installed to meet the present demands. Each screen consists of a circular disk 22 ft. in diam., inclined at an angle of  $15^\circ$  with the horizontal, furnished with a truncated cone in the center, and perforated with slots  $2\frac{1}{2}$ " long and  $\frac{3}{16}$ " wide. Description of the construction is given. G. C. BAKER

**The sewage disposal plant at Heidenau.** ANON. *Städtereinigung* 7, 40; *Wasser u. Abwasser* 15, 30-1(1921).—Heidenau, a village of 6,500 population, has a plant consisting of Travis tanks, with a flowing through velocity of 2.5 min. per sec., preceded by a coarse screen and a grit chamber. Sludge storage capacity is provided for 3.5 months. F. W. MOILMAN

**Power from sewage settling tanks.** G. STRASSBURGER. *Gesundh. Ing.* 42, 329-37 (1919); *Wasser u. Abwasser* 15, 27-9(1921).—S. proposes to trap the gases given off in an Imhoff tank by certain modifications in design. He calculates that for a plant the size of that at Erfurt, population 130,000, over 300,000 cu. m. of gas would be produced annually, which should generate 270,000 kw. hrs. F. W. M.

**The recovery of fat from sewage in Austria.** ANON. *Städtereinigung* 11, 74-6; *Wasser u. Abwasser* 15, 168(1921).—During the war 1328 Boverman fat traps were installed in Austria. In Vienna 33 kg. of purified fat were recovered per trap per year. The crude fat was dewatered as far as possible by being heated to  $85^\circ$  in steam-heated vats. Then from 2 to 5% of 1:4  $\text{H}_2\text{SO}_4$  was added, and the fat skimmed. NaCl or fullers earth was used to clarify it. The purified fat had acid nos. from 20 to 196, sapon. nos. from 182 to 217 and I nos. 31 to 50. The fatty acids slowly increased on standing. The fats were used for army soap and washing powders. F. W. M.

**Fluctuations in the chemical composition of city sewage.** W. MÜLLER. *Z. Ver. Gas u. Wasserfach in Österreich u. Ungarn* 58, 289-98; *Wasser u. Abwasser* 15, 111(1921).—The compn. of sewage depends to a great extent on the compn. of the drinking water, but is not greatly affected by the inclusion or exclusion of human excreta, contrary to

the usual belief. Street washings are usually more polluted than household sewage. Tables show daily, weekly and yearly fluctuations in compn. of representative sewages.

F. W. M.

**The clarification plant at Stuttgart.** MAIER AND SOHLER. *Gesundh. Ing.* **42**, 393-408; *Wasser u. Abwasser* **15**, 33(1921).—The sewage of 315,000 people, with an av. flow of 120 l. (31.7 gal.) per capita per 24 hrs., is treated in Imhoff and Neustadt (sep. digestion) tanks. The sludge compartments were designed for a storage of 0.3 l. per capita per 24 hrs., 50% higher than that used in the Emschergerossenschaft. The total settling capacity of the Imhoff tanks is 1685 cu. m.; of the Neustadt tanks 1564 cu. m. The capacity of the Imhoff sludge compartments is 5980 cu. m.; of the Neustadt 6760 cu. m. Sludge beds 145 acres in area are provided.

F. W. M.

**Installations for the burning of street wastes.** ANON. *Gesundh. Ing.* **45**, 286 (1922).—A table is given summarizing the answers to a questionnaire. Information as to the make of incinerators used, amt. of material burned, av. heat value, seasonal changes in the heat value, uses of the heat and the by-products is given in considerable detail.

MARTIN E. FLENTJE

**Keeping fresh water and air in city drainage systems.** V. HANFFSTENGEL. *Gesundh. Ing.* **45**, 367-9(1922).—An attempt should be made to keep the sewage, in each drainage system, fresh; and to have as many complete changes of air as possible. Sewage is maintained fresh by having a high rate of flow, over a short distance, to the place of purification. The rate of flow is dependent on the relative fall,  $h/l$ , and the hydraulic radius. Sixty cm. per sec. has been found to be the lowest rate at which floating material will not settle out. A table for various values of diam. of pipe and the relative fall at which this lowest rate is just attained is given. "Dead points," at which solids collect, necessitates cleaning, either by mech. means or flushing, the effectiveness of which depends on the vol. of flushing water per sec., duration, and rate of flow. Mixt. of atm. air with the sewer air decreases the common "sewer-gas" nuisance.

MARTIN E. FLENTJE

**Equalization or storage basins in city drainage.** O. SPIEGELBERG. *Gesundh. Ing.* **43**, 6-9, 23 5, 29-31, 169-78(1920); *Wasser u. Abwasser* **15**, 178-81(1921).—A detailed discussion of the use of storage basins for storm water flows, with numerous examples.

F. W. M.

**Drainage of cities on the Niederheim.** W. KRAWINKEL. *Gesundh. Ing.* **45**, 265-6(1922).

MARTIN E. FLENTJE

**Index of toxicity from lighting and heating apparatus and from explosive motors.** KOHN-ABREST. *Compt. rend.* **174**, 1046-8(1922); cf. Florentin and Vandenbergh, *C. A.* **15**, 1268.—The index proposed is the ratio of the vol. of CO to the vol. of CO<sub>2</sub> in the product of combustion. The indices found in 11 combustions varied from 0.0015 to 14.0. Exhaust gases from motors gave the highest indices and are decidedly dangerous. For habitations an index of 0.01 to 0.02 may be considered safe. CO was estd. by the blood method of Ogier and Kohn-Abrest.

L. W. RIGGS

**Disinfection experiments with Koro-Noleum and Phenokko.** WEDEMANN. *Disinfektion* **1921**, No. 10; *Arb. Reichsgesundh.* **53**, 91-4(1922).—A report of expts. with two commercial disinfectants.

F. W. T.

CLAR, WILHELM: *Wasserversorgung und Abwasserbeseitigung*. Potsdam and Lypzig: Bonnez & Hachfeld. M 3.25. 24 pp.

HALBFASZ, WILH.: *Grundlagen der Wasserwirtschaft*. Berlin: Gebr. Bornträger. M 32. 154 pp. Reviewed in *Gas u. Wasserfach* **65**, 13(1922).

WALTER, PAUL: *Erdsalzgehalt des Trinkwassers und Kariesfrequenz in der Schweiz*. Zürich: Berichthaus. 39 pp.

WHYATT, H. GILBERT: *Sewers and Sewage*. London: Sir Isaac Pitman & Sons, Ltd. 2s. 6d. Reviewed in *Engineering* 113, 630(1922).

Boiler-scale preventive. O. L. K. ANDERSEN. U. S. 1,416,925, May 23. NaOH 25, mangrove bark 10, gambier 10, catechu 30 and potato water 25 parts.

## 15—SOILS, FERTILIZERS AND AGRICULTURAL POISONS

J. J. SKINNER

Progress in the field of agricultural chemistry. O. ENGELS. *Fortschritte Chem.* 16, 151-73(1921); 17, 83-110.—Progress from July 1919 to July 1921. C. C. DAVIS

Report on soils. W. H. MACINTIRE. *J. Assoc. Official Agr. Chem.* 5, 405-18 (1922); cf. *C. A.* 16, 604.—The 6 following procedures for the detn. of total S in soils were studied: (1) peroxide combustion, (2)  $Mg(NO_3)_2$  combustion, (3) aqua regia digestion, (4)  $HNO_3$  digestion, (5)  $Mg(NO_3)_2$ ,  $CaCO_3$ ,  $NH_4Cl$  combustion, (6)  $CaO$  combustion. The results obtained by collaboration are given, these methods being used. The peroxide combustion and  $Mg(NO_3)_2$  combustion gave varying results. The  $Mg(NO_3)_2$ ,  $CaCO_3$ ,  $NH_4Cl$  procedure is not applicable to all soils. The  $HNO_3$  digestion is preferred to the aqua regia digestion because of the smaller amts. of dissolved Fe to be removed. A wet method is desirable in that it leaves the insol. residue in such a condition as to facilitate filtration and washings. RUSSELL M. JONES

The use of microorganisms for the determination of the content in the soil of plant food available for higher plants. K. A. BONDORFF. *Den. Kgl. Veterinar Z. Landbohøjskoles Aarskrift* 1918, 339-62; *Physiol. Abstracts* 6, 167.—A soln. of mannitol inoculated with a sample of soil develops an azotobacter membrane when the quantity of  $CaCO_3$  is sufficient, but not when the soil needs  $CaCO_3$ . The  $CaCO_3$  in this reaction acts as a buffer, keeping the H-ion concn. near the neutral point, which is a necessary condition for the development of azotobacter. This bacterium is killed at  $pH$  6.7. The use of *Aspergillus niger* as a measure for the content of phosphates available in soils is studied and it is concluded that this method cannot be used. R. M. JONES

The fertilizer industry in the United States. JACOB G. LIPMAN. *Chimie et industrie* 7, 1001-8(1922).—An address. A. P. C.

Supply of German nitrogen requirements before and after the war. H. W. SCHMIDT. *Umschau* 26, 327-8(1922).—Statistics are given of the fertilizer sources of Germany for 1913 and for the past year. At present less than half the combined N necessary for agricultural purposes can be furnished by farm manures. To this may be added the  $NH_3$  from coking of coal, leaving 390,000 tons per year to be furnished by the fixation of atmospheric N. L. W. RIGGS

Report of committee on methods of sampling fertilizers to cooperate with a similar committee of the American Chemical Society. C. H. JONES, E. G. PROULX AND B. F. ROBERTSON. *J. Assoc. Official Agr. Chem.* 5, 315(1922).—It is recommended that (1) a sampler be used that removes a core from the bag from top to bottom; (2) at least one pound of material constitute an official sample; (3) the entire sample be passed through a 10-mesh sieve previous to its subdivision for analysis; (4) cores be taken from not less than 10% of the bags present, unless this necessitates cores from more than 20 bags, in which case a core shall be taken from one bag from each additional ton represented. RUSSELL M. JONES

The manufacture of fertilizers. L. CARPENTER. *Chem. Age* (London) 6, 620-1 (1922).—A review with special reference to the coking and mechanical handling of fertilizers. RUSSELL M. JONES



**Availability of some nitrogenous and phosphatic materials.** G. S. FRAPS. Texas Agr. Expt. Sta., *Bull.* 287 (1922).—Pot expts. were conducted with 5000 g. of soil, acid phosphate,  $K_2SO_4$  and 0.1 g. of N as ground charred wheat being added. The N of the wheat showed but slight fertilizer value. The availability of the N of cottonseed meal alone and with the addition of  $CaCO_3$ , also the N of cyanamide, muck tankage and horn and hoof meal were compared in pot tests. Although the  $CaCO_3$  increased the nitrification of cottonseed meal when added to the soil with the meal, less N was taken up by the sorghum, av. 28.6%, than when the meal was used alone, av. 32.6%. The av. results with cyanamide were 35.9%, with muck tankage 3.0% and with horn and hoof meal 27.8%. Considerable variations were found on the different soils. Duplicate expts. were made with corn on soil in pots testing the availability of mineral phosphates. The  $P_2O_5$  of rock phosphate in 1 test was not taken up at all. The  $P_2O_5$  of vivianite had about 33%, that of triplite about 25%, while wavellite and dufrenite had about 10% of the availability of acid phosphate. Data are also given showing the % of  $P_2O_5$  recovered in corn and sorghum for 1913 and 1914 from acid phosphate, crude phytin and a  $H_2O$  ext. of phytin. The av. results were 62% for acid phosphate, 53% for crude phytin and 24% for the  $H_2O$  ext. of phytin. Measured by the 1st-year crop alone the  $P_2O_5$  of crude phytin is about 50% as available as that of acid phosphate. Comparing cottonseed meal and acid phosphate, the  $P_2O_5$  was taken up to the greater extent from the former material. The availability of the  $P_2O_5$  of basic slag varied from 45 to 94% on 6 soils with 3 crops. If the first crops only were considered the rank of the basic slag would be lower.

F. C. COOK

**The Woburn Experimental Station of the Royal Agricultural Society of England.**

**Pot culture experiments.** J. A. VOELCKER. *J. Roy. Agr. Soc. England* 82, 286-97 (1921).—In pot culture expts. Cr as chromate or dichromate in amts. of 0.005% was harmful to wheat. Quantities less than this were beneficial.  $CrCl_3$  was harmful in amts. from 0.005 to 0.0005%.  $Cr_2(SO_4)_3$  in these amts. had no effect.  $H_2CrO_4$  was at first harmful but became stimulating.  $CaSiO_3$  and Mg silicate in amts. of 1-4 tons per acre gave a good increased yield with wheat. Kaolin had no effect. 0.1% P as  $KF$  was very beneficial while the same amt. of  $NaF$  killed the plants; 0.05% produced stimulation. The results of the effect of other miscellaneous material are reported.

J. J. SKINNER

**The effect of rock phosphate upon the corn possibility of the phosphoric acid of the soil.** G. S. FRAPS. Texas Agr. Expt. Sta., *Bull.* 289 (1922).—Corn and sorghum were grown in pot expts. in 5000 g. of soil low in active  $P_2O_5$ . One g. of  $NH_4NO_3$  and 1 g. of  $K_2SO_4$  were added to each pot. The expts. were undertaken to test the effects of rock phosphate upon the  $P_2O_5$  removed by the plants. With no phosphate added, 5.5 p. p. m. of  $P_2O_5$  were removed per crop (av. of 50 crops on 25 soils). With the addition of 1 ton of rock phosphate, equal to about 300 p. p. m. of  $P_2O_5$ , 9.4 p. p. m. of  $P_2O_5$  were removed. The av. % of  $P_2O_5$  removed from rock phosphate is 1.3 and from soil phosphates 0.5 to 1.75. Increasing the  $P_2O_5$  added in rock phosphate from 300 to 600 p. p. m. increased the  $P_2O_5$  removed per crop only 0.63 p. p. m. The % of added  $P_2O_5$  removed per crop was 1.4 for 300 p. p. m. and 0.8 for 600 p. p. m. with the same crop and the same soil. The % of added  $P_2O_5$  removed per crop was 1.43 when 1 ton of rock phosphate per acre was added, 0.8% when 2 tons was added and 0.5% with the addition of 4 tons. The addition of rock phosphate in amts. greater than 1 ton per acre has little effect on the amt. of  $P_2O_5$  removed by the crops. Soft Florida phosphate is slightly more effective than hard Tennessee phosphate. The % of  $P_2O_5$  removed was 1.98 for the former and 1.52 for the latter. The amt. of  $P_2O_5$  removed from  $Ca_2HPO_4$  is much greater than from rock phosphate. The  $P_2O_5$  of rock phosphate is almost all sol. in 0.2 N  $HNO_3$  as used in soil analysis. The  $P_2O_5$  added to the soil in rock phos-

phate does not represent as highly available  $P_2O_5$  as is represented by the active  $P_2O_5$  already present in the soil.

F. C. COOK

**Changes in the composition and cost of fertilizers in New York from 1914 to 1921.**

L. L. VAN SLYKE. New York Agr. Expt. Sta., *Bull.* 493, 12 pp.(1922).—A review of the fertilizer market from 1914 to 1921. In 1914, 1004 different fertilizers occurred on the market, which dwindled to 561 in 1918. The number has gradually increased since 1918, and in 1921, 742 were found. The av. % of N remained uniform until 1918, being about 2.2% each year, but this dropped in 1918 to 2.02% and in 1920 to 1.81%. In 1921 there was an increase to 2.07%. The % of  $P_2O_5$  increased during the first 3 years and has since decreased somewhat. In 1914 the av. % of K in complete fertilizers was about 6; this decreased in 1915 to about 3, and in 1916 to 1.32. In 1920 the av. K was 3.24% and in 1921, 3.62%. A table is given showing the av. retail price per ton of fertilizer from 1914 to 1921.

J. J. SKINNER

**Report on insecticides and fungicides.** J. J. T. GRAHAM. *J. Assoc. Agr. Official Chem.* 5, 392-404(1922).—A study was made of methods for the detn. of total As,  $As_2O_3$ , CaO in  $Ca_3(AsO_4)_2$ ; for the detn. of  $As_2O_3$  and ZnO in  $Zn_3(AsO_4)_2$ ; and for the detn. of PbO, ZnO and Cu in a mixt. of Bordeaux,  $Pb_3(AsO_4)_2$  and  $Zn_3(AsO_4)_2$ . Methods are also considered for the detn. of  $As_2O_3$  in Paris green, total As in London purple and MgO in  $Mg_3(AsO_4)_2$ . Tables give results obtained by collaborators. R. M. JONES

Possible utilization of some sands of Montescaglioso (PARLATI) 19. Phosphate ores (PIETRKOWSKI) (GOLDSCHMIDT) 18. The employment of pure cultures of micro-organisms in agriculture (RAHN) 16.

ILS, ALBERT: *Wirkung und Anwendung der natürlichen und künstlichen Düngemittel*. Biberach a. Riss: Bopp & Haller. 18 pp. M 3.

SACHSSE, R. and HABERKNOLL, E. *Kurzgefasster Leitfaden der landwirtschaftlichen Chemie*. 7th Ed. revized by Rudolf Sachsse and Fr. Kretzschmar. Bautzen: Emil Hühners Verlag. M 16. Reviewed in *Z. angew. Chem.* 35, 236(1922).

SCHNIDEWIND, WILHELM: *Die Kalidüngung*. 4th Ed. revized. Berlin: P. Parey. 72 pp. M 25.

**Soil mixture for forced growing of potatoes.** J. HUSSON. U. S. 1,417,248, May 23. Sand is mixed with a fertilizer contg. N 2-3%, sol. phosphate 3-4% and potash 1-2%.

**Apparatus for drying fertilizers.** P. J. HAMLER. U. S. reissue 15,362, May 23. Original pat. 1,321,628.

**Arsenical insecticide.** H. H. DOW. U. S. 1,417,232, May 23. Pb acetate or other sol. Pb compd. is reacted upon with an excess of arsenic acid and the residual acid is neutralized with  $Mg(OH)_2$ ,  $Ca(OH)_2$  or  $Ba(OH)_2$ .

## 16—THE FERMENTATION INDUSTRIES

C. N. FREY

**The employment of pure cultures of microorganisms in industry and agriculture.** OTTO RAHN. *Naturwissenschaften* 10, 241-6(1922).—Recent applications of pure cultures to the EtOH, beer, rum, baking, citric acid, butter, cheese and pickling industries and to agriculture are described.

C. C. DAVIS

**Determination of the diastatic activity of malt.** W. WINDISCH AND P. KOLBACH. *Wochschr. Brau.* 38, 149-51(1921); *Chimie et industrie* 7, 984(1922).—The following

modification of J. L. Baker and H. F. E. Hulton's method (*C. A.* 15, 1778) is proposed. Digest 25 g. of finely ground malt (or broken malt in the case of green malt) in 500 cc. of water at 50° for 30 min. To 100 cc. of a 2% soln. of Kahlbaum's sol. starch in a 200-cc. volumetric flask add 5 cc. of malt ext. dild. with an equal vol. of water (for green malt), or 5 cc. of undild. ext. (for pale malt), or 10 cc. of ext. (for dark malts), shake thoroughly, let stand 30 min. in a water-bath at 20°, add 10 cc. of 0.1 *N* NaOH, make up to vol., and shake. Place 30 cc. of this soln. in an Erlenmeyer flask, add 20 cc. of standard I and 30 cc. of 0.1 *N* NaOH, let stand 10 min. at room temp., add 4 cc. *N* H<sub>2</sub>SO<sub>4</sub>, and titrate the excess of I with 0.05 *N* Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. 1 cc. 0.05 *N* I = 855 mg. maltose. A blank must be run. The diastatic value is expressed as the number of g. of maltose formed by the diastase contained in 100 g. of malt. The method gives satisfactory results if the instructions are strictly adhered to. A. P.-C.

**Manufacture of mannitol.** PIERO FENAROLI. *Giorn. chim. ind. applicata* 4, 85-9(1922).—Dissolve 1 part by wt. of molasses from manna at 37° in 5-6 parts H<sub>2</sub>O contg. 1% 66° B<sub>é</sub>. H<sub>2</sub>SO<sub>4</sub> boil for 1 hr., then neutralize with powdered marble and filter while hot. Cool, begin fermentation by direct addn. of alc. ferments, making the medium a little acid according to the strain of ferment used. When the fermentation is finished (it may be profitably protracted unless acetic fermentation begins), conc., and finally purify the cryst. residue by the methods applicable to crude manna. Mannitol may be formed synthetically from mannose by the use of H at 50 atm. pressure in the cold and successive heating with nicked pumice at 120° for 12 hrs. The sepn. of mannitol from a soln. contg. NaOH or Na<sub>2</sub>CO<sub>3</sub>, without recourse to the use of alc., is based upon the transformation of the Na to neutral sulfate and sepn. of the Na salt and of the mannitol by direct crystn. between detd. limits of temp.: Conc. the soln. by boiling at ordinary pressure, when the Na<sub>2</sub>SO<sub>4</sub> seps. directly as anhydrous salt from the boiling liquid. Filter while hot. The mannitol seps. out as the liquid cools down to 32-3°.

ROBERT S. POSMONTIER

**Fermentation of blackberry juice (*Robus fruticosus*).** P. BERTOLD. *Giorn. chim. ind. applicata* 3, 492-3(1921).—Pressed juice of blackberries filtered through cloth was allowed to ferment spontaneously over a period of 2 months, although the main action took place in the first 2 weeks. The wine produced was limpid, dull red, of agreeable odor and of a slightly sharp taste. On analysis it showed these results:  $d_{44} = 1.031$ , alc. = 4.5% (5.60 by vol.), total acidity as tartaric acid = 0.098, ext. = 9.15, K acid tartrate = 0.189, free tartaric acid = small amt., reducing sugar = 2.57, ash = 0.71, glycerol = 0.62, tannic substances = 0.70, citric acid = small amount. The wine, kept for a long time in divided vessels, does not undergo acetic fermentation, or change its content of alc. A sample of the original juice, after boiling for 3 hours and bringing back to vol. with H<sub>2</sub>O, showed a gravity of 1.185, acidity (as tartaric acid) = 0.33%, and reducing sugar = 12.75, whereas the unboiled pressed juice contained only 8.80 reducing sugars. The boiled redild. juice was subjected to spontaneous fermentation as before, and gave a wine of the following compn.:  $d_{44} = 1.029$ , alc. = 5.59% (7.00 by vol.), total acidity = 0.90, volatile acidity = 0.095, ext. = 8.90, reducing sugar = 2.30.

ROBERT S. POSMONTIER

**Detection of saccharin and dulcin in beer.** A. BAUMANN. *Z. Ges. Brauw.* 1920, 137; *Giorn. chim. ind. applicata* 4, 69-70(1922).—Treat beer with milk of lime and evap. to dryness. Take up the residue with alc. and pour the whole onto a satd. soln. of NaCl. After stirring, allow to rest, and filter. Evap. the liquid to  $\frac{1}{3}$  to drive off alc., wash with petroleum ether, shake with Et<sub>2</sub>O to ext. dulcin. Exam. for dulcin in the ethereal ext. after recrystg. from alc., by treating with a dil. soln. of Hg(NO<sub>3</sub>)<sub>2</sub>, heating on the water bath for  $\frac{1}{4}$  hr., and adding a small amt. of PbO<sub>2</sub>; dulcin gives a violet coloration. The saccharin, held in soln. as Ca saccharinate insol. in Et<sub>2</sub>O, is

set free by acidifying with dil.  $H_2SO_4$  and extg. with a mixt. of equal parts of  $Et_2O$  and petroleum ether. Test for saccharin in the ext. by the usual methods. R. S. P.

The alcohol problem in Germany. *Rev. prod. chim.* 25, 289-92(1922).—A brief discussion of the struggle between the mfrs. of agricultural alc. and of synthetic alc., with a brief sketch of the present status of the synthetic alc. industry. A. P.-C.

GABER, AUGUST: Die Likör-Fabrikation. 10th Ed. revized by J. Pardeller. Vienna and Leipzig: H. Hartleben. 351 pp. M 48.

Lactic fermentation of fruit juices. J. C. RICHARD. U. S. 1,417,412, May 23. Fruit juices (such as pineapple or prune juice) are subjected to fermentation with *Bacillus bulgaricus* in order to obtain palatable medicinal compns.

## 17—PHARMACEUTICAL CHEMISTRY

W. O. EMERY

Is the undecomposed hydrogen peroxide or the oxygen split from it the carrier of disinfecting action? A. MÜLLER. *Z. Hyg. Infektionskrankh.* 93, 348-71(1921).—Cultures of *B. coli* were prepd. contg. varying amts. of catalase, and consequently varying amts. of  $O_2$  split by the catalase from added  $H_2O_2$ . In none of these cultures were differences noted in the bactericidal action that could be ascribed to the differences in  $O_2$  content. Expts. in which the  $H_2O_2$  content, catalase content and H-ion concn. were carefully controlled showed that the bactericidal action of  $H_2O_2$  rests not on the  $O_2$  liberated from  $H_2O_2$  but on the undecompd. peroxide itself. The presence of catalase in a measure protects the organism against the action of  $H_2O_2$ . F. A. CAJORI

Metal tubes for cosmetics. A. BEYTHIEN. Dresden. *Z. Nahr. Genussm.* 43, 47-55(1922).—The corrosive action of various pastes and cosmetics on metal tubes was studied. Quantities of Pb ranging from a trace to 0.0022% were imparted to pastes by tinned lead tubes. In the same pastes the Sn content varied from 0.0028 to 0.1160%. Sn was most readily dissolved by alk. pastes. The subject is discussed from a regulatory viewpoint. D. B. DILL

Aloes from Eritrea. ANON. *Giorn. farm. chim.* 71, 57-64(1922).—A sample of aloes from Eritrea, an Italian colony in Africa, gave the following analysis:  $H_2O$  8.0, aq. ext. 64.25, inert resin 27.75, ash 1.31, pharmacologically active matter 71.50, aloin 22.70, emodin 0.33%. A. W. DOX

Synthetic medicinal chemicals manufactured in America. A. S. BURDICK. *Chem. Age* (N. Y.) 30, 221-3(1922).—A brief account of the development of this new industry in America, together with mention of the principal synthetics (arsphenamine, aspirin, acetanilide, barbital, luminal, cinchophen, procaine, anesthesin, orthoform, sulfonal, trional, etc.) produced and by whom manufd. W. O. E.

Essential oil from *Blumea malcomii*. J. J. SIMONSEN AND M. G. RAU. *J. Chem. Soc.* 121, 876-83(1922).—This oil, obtained from the herb by steam distn. in a yield of about 0.25%, resembles caraway-seed oil somewhat in odor. It consists almost entirely of 2 ketones, *d*-carvotanacetone ( $\Delta^4$ -menthen-2-one) and *l*-tetrahydrocarvone (*p*-menthan-2-one); the former constitutes about 82% by wt. of the oil, the latter about 16%. A trace of a phenol was also isolated together with a mixt. of fatty acids and sesquiterpenes, insufficient, however, for identification. The occurrence in nature of carvotanacetone would not appear to have been previously definitely established. It is probable that the tetrahydrocarvone is formed in the plant by the reduction of the

*d*-carvotanacetone, during which process a change in rotation takes place. Cf. Vavon (C. A. 5, 3224) on the reduction of *d*-carvone to *d*-carvotanacetone and finally to *l*-tetrahydrocarvone. W. O. E.

**Sudan essential oils.** A. F. JOSEPH AND B. W. WHITFIELD. *J. Soc. Chem. Ind.* **41**, 144-5T(1922).—*Naal* oil is distd. from *Andropogon schoenanthus* var. *nervatus* (now *Cymbopogon nervatus*, Chiov.), the yield obtained with H<sub>2</sub>O or steam varying from 0.8 to 1.5% of the wt. of the dried grass. The light yellow oil did not darken perceptibly on keeping in diffused light for 2 years; in odor it closely resembles the oil of ginger grass, somewhat also in its physical properties. The chem. consts. of the two are, however, quite different. Distn. of the oil both at the ordinary and under diminished pressure is difficult owing apparently to some mol. condensation or other rearrangement. The oil appears to consist mainly of *l*-limonene and perilla alcohol, and differs so entirely from that described by Schimmel & Co. (cf. C. A. 5, 3495) that it is doubtful whether this firm actually worked with genuine "Naal" grass at all. Further investigation of the oil is contemplated. W. O. E.

**Sudan essential oils.** A. F. JOSEPH AND B. W. WHITFIELD. *J. Soc. Chem. Ind.* **41**, 172T(1922).—A specimen of the dried rhizomes of *Cyperus rotundus* (a sedge) gave 0.5% of an aromatic oil in which the odor of camphor could be detected. The consts. were:  $d_{20}^{20}$  0.9548;  $[\alpha]_D^{20}$  -19.9°;  $n_D^{25}$  1.4967; acid no. 1.0; sapon. no. 6.6 (105 after acetylation); soly. in 80% alc. 1 in 4; soly. in 70% alc. nil. W. O. E.

**The stability of arspenamine solution.** PETER MASUCCI. *Am. J. Pharm.* **94**, 338-41(1922).—Arsphenamine solns. can be kept under N gas at ice-box temp. for 4 months without noticeable change of color, increase in oxidation or toxicity. Solns. kept under N but at room temp. begin to show a change in color from yellow to a reddish tinge in about 2 weeks; at the end of 8 weeks about 10% becomes oxidized with a very noticeable increase in toxicity. The exptl. data indicate very clearly that the temp. at which solns. are kept is a very important factor. The oxidation of arspenamine to a so-called "arsenoxide" takes place much more rapidly at room temp. than at ice-box temp. This fact might be used in the prepn. of arspenamine solns. for intravenous injections where a certain amt. of shaking is necessary in order to get the drug in soln. Shaking at low temp. should not cause any material increase in toxicity. W. G. GAESSLER

**The oil of *Agastache pallidiflora*.** J. F. COUCH. *Am. J. Pharm.* **94**, 341-3(1922).—The essential oil of this plant was investigated as a possible source of thymol or menthol. Steam distn. of flowering heads yielded 0.155-0.316% of dry oil, having a yellow color and a very penetrating peppermint odor with some marked suggestion of thyme. The leaves yielded 0.083% of dry oil, having a rank thyme odor only. None of the samples of oil, nor any of the aq. distillates contg. dissolved oil affected FeCl<sub>3</sub> soln. and all were neutral to litmus. The following physical consts. were detd. for the oil from the flowers:  $d_{20}^{20}$  0.91924,  $[\alpha]_D^{25}$  -8.60°,  $n_D^{25}$  1.4865. The oil is sol. in the ordinary solvents. On cooling to -10° and letting stand at that temp. for several hrs. there was no sepn. of any cryst. material. Consequently the amt. of free menthol present cannot be very large. Phenols were tested for by the usual absorption method with 5% NaOH. The vol. of oil diminished slightly, but on acidifying and shaking out the aq. layer with ether, no phenols were found. Pulegone and other ketones were absent. W. G. GAESSLER

**Variations in the hydroxymethylanthraquinone compounds in black alder and their galenical preparations.** R. MAURIN. *Bull. sci. pharmacol.* **29**, 175-80(1922).—An inquiry in the cause of the variability in purgative action of various preps. of black alder based on the idea that the hydroxymethylanthraquinones, free and combined, are the most active principles of the plant. Bark from young branches contains more of both groups than does that from old ones, although very young plants have but little.

A report is also made of the relative amt. of these compds. according to geographical distribution. There occurs a decrease in the amt. of combined anthraquinones as the interval between collection and analysis is increased, i. e., the potency decreases with storage. A test for the detn. of the best method of prepn. showed that the fluid ext. is better than the  $H_2O$  ext. The tincture is much better than either while infusions or decoctions are quite unsatisfactory.

F. S. HAMMETT

**The liquorice extract industry.** EM. DÉPASSE. *Chimie et industrie* 7, 886-8 (1922).—Brief description of the com. process used for the extn. of liquorice.

A. P.-C.

**Defects of the existing process of industrial production of licorice.** P. BERTOLD. *Giorn. chim. ind. applicata* 3, 490-2 (1921).—Variations in the quality of com. licorice are due to the inefficient process used in producing it. The principal cause of the excessive quantity of ash in many samples of ext. of licorice is the poor washing of the licorice root before manuf. An ext. produced by boiling the root directly with water, and an ext. produced from roots previously macerated for 2 hrs. gave, resp.,  $H_2O$  16.05, 16.28; insol. residue 28.30, 25.56; ash 8.15, 6.08. Another factor influencing the high insol. residue and ash is the use of ordinary, generally hard water instead of water of condensation. This factor also accounts for the low glycyrrhizin values of the com. exts. Equal quantities of roots boiled, resp., with distd.  $H_2O$  and ordinary  $H_2O$  gave exts. analyzing:  $H_2O$  15.38, 14.87; insol. residue 0.54, 0.86; ash 5.25, 6.38; glycyrrhizin 19.22, 12.03. The use of direct firing for boiling and concg. results in lack of homogeneity and brilliancy in the ext., and gives to it a characteristic burnt odor. ROBERT S. POSMONTIER

**Chrysanthemum powder.** D. COSTA. *Giorn. chim. ind. applicata* 4, 91-3 (1922).—Review, including toxin of the drug and analysis of the powder ext. R. S. POSMONTIER

**Vitex as a rival of quinine.** VAUGHAN. *Brit. Med. J.* 1921, 186; *Chemist and Druggist* 94, 903 (1921).—Infusions and exts. of the leaves or bark of *Vitex peduncularis*, Wall., var. *Roxburghiana* are useful in malarial fevers. The drug is non-toxic, not bitter, mildly stimulant, diuretic and does not seem to depress the heart. Infusions with hot  $H_2O$  are of 3 strengths: 1 in 40, 2 in 40 and 4 in 40. A concd. infusion of the leaf is made by percolating for a week powd. leaf 8 oz. with 90% EtOH 2.5 oz. and  $CHCl_3$ - $H_2O$  to make 12 oz. Fresh stem bark ext. is made by percolating ground bark 4.5 oz. with 90% EtOH 6 oz. and  $CHCl_3$ - $H_2O$  to make 30 oz.

S. WALDBOTT

**Tuba root.** ANON. *Chemist and Druggist* 95, 41 (1921); cf. *C. A.* 11, 2370.—An account of its uses, its botany and chem. properties. M. Greshoff (1890) found 5% of a resinous acid, *derrid*, poisonous to fish. L. Wray (1892) obtained 9.42% of "tubain," a mixt. contg. the active principle. F. B. Power (1902) found the  $CHCl_3$ -sol. part of the resin analogous to "derrid." The root is also believed to be an insecticide (*C. A.* 13, 2723).

S. WALDBOTT

**The medicinal value of essential oils.** R. M. AND J. GATTEFOSSÉ. *Chemist and Druggist* 95, 116 (1921).—An example is *afrol*, a "combination of wild thyme and pine" found useful in treating the foot-and-mouth disease.

S. WALDBOTT

**Cadet de Gassicourt, Charles-Louis, 1769-1821.** ANON. *Chemist and Druggist* 95, 658 (1922).—Biographical.

S. WALDBOTT

**The keeping properties of aspirin and aspirin tablets.** A. J. JONES. *Chemist and Druggist* 95, 749-50 (1921); cf. *C. A.* 13, 1741; 14, 2963, 3124.—The Brit. Pharm. test for a negative reaction for free salicylic acid in aspirin cannot be met. A limit of 0.15% is reasonable for recently made com. samples, and 0.3% allowing for long storage, an amt. which well made aspirin will not exceed. In tablets, 0.2% free salicylic acid is a proper standard; 0.4% should not form within, e. g., 6 months; after this time, or when poorly stored, or exported, no guarantee can be given. The detn. of acid and

ester nos. and Br absorption are additional and important aids in judging the quality of aspirin tablets. S. WALDBOTT

**Franciscus Mercurius Van Helmont.** W. MASEKEW. *Chemist and Druggist* **95**, 854(1921).—Reproduction of a portrait now in the National Gallery, and short biography of the younger Van Helmont. S. WALDBOTT

**Absorption of volatile oils by fatty acids.** C. A. COFMAN-NICORESTI. *Chemist and Druggist* **95**, 854-5(1921); cf. *C. A.* **11**, 1882, 2388.—Salts of higher fatty acids, when dissolved in a volatile liquid at a concn. of 5% or more, crystallize in the form of a spongy mass which retains the whole of the solvent. The use of polarized light in examn. is suggested. S. WALDBOTT

**Essential oils constituents.** L. G. RADCLIFFE. *Chemist and Druggist* **96**, 382, 416-7, 482(1922).—Abstr. of three ("Cantor") lectures. S. WALDBOTT

**Javanese essential oils.** J. J. B. DEUSS. *Sluyter's Monthly; Chemist and Druggist* **96**, 461(1922).—Among the various oils described are citronella, lemongrass, palmarosa, patchouli, cinnamon and cajuput oils. S. WALDBOTT

**Preparation of citrate and tartrate of bismuth.** FABRÈGUE. *J. pharm. chim.* **25**, 341-4(1922).—These 2 salts, rendered sol. by alkali carbonates or by  $\text{NH}_4\text{OH}$ , are to replace the insol. emetic salt of Bi, used as an antisiphilitic. Dissolve 100 g.  $\text{Bi}(\text{NO}_3)_3$  in glacial  $\text{AcOH}$ , add 500 cc.  $\text{H}_2\text{O}$  and filter. Then add a soln. of 67 g. Na citrate in 600 cc.  $\text{H}_2\text{O}$ . Decant the white ppt. and wash it with 90%  $\text{EtOH}$  until  $\text{EtOH}$  leaves no residue upon evapn. Dry at about  $60^\circ$ . Bi citrate (A) is a white, microcryst. powder, insol. in  $\text{H}_2\text{O}$ ,  $\text{EtOH}$ ,  $\text{Et}_2\text{O}$ , dil. acids, but sol. in dil.  $\text{NH}_4\text{OH}$ ; it contains 58.43%  $\text{Bi}_2\text{O}_3$ . For intramuscular or perhaps also intravenous injections, put 0.5 g. of A into a sterile flask, add drop by drop 10% sterile  $\text{NH}_4\text{OH}$  soln., boil to expel excess of  $\text{NH}_3$ , filter and fill up to 10 cc. To prep. Bi tartrate (B) use 97 g. Na tartrate in place of the above 67 g. Na citrate. B contains 45.99%  $\text{Bi}_2\text{O}_3$ . S. WALDBOTT

**Hypophysis and its posterior lobe considered pharmacologically.** V. BORRIEN. *J. pharm. chim.* **25**, 344-8(1922).—The active principle of the posterior lobe is very diffusive in  $\text{H}_2\text{O}$  and  $\text{EtOH}$ , is analogous in compn. to adrenaline, but thus far has not been isolated. To preserve the lobes for several days after collection, weigh, then immerse them in a small amt. of physiol. 0.7% soln. to which 0.5%  $\text{PhOH}$  and 5 to 6 drops of  $\text{AcOH}$  per 100 cc. are added, and keep the prepn. in a well corked flask. S. WALDBOTT

**The limits of exactness of the physiological control method for adrenalin.** A. RICHAUD. *J. pharm. chim.* **25**, 369-73(1922).—Three successive injections each of 0.03 mg. of adrenaline into the same animal, at 8 min. intervals, gave, resp., 7.7, 9.2 and 9.9 cm. instead of equal increase of pressure (cf. *C. A.* **16**, 2385). The habitual av. error in Cushny's method varies between 20 and 30%. Still, this method of detg. adrenaline content will remain very valuable in the hands of the experienced. S. WALDBOTT

**Preparation and preservation of colorless solutions of eserine salicylate.** L. DRÉBUCQUET. *J. pharm. chim.* **25**, 373-5(1922).—Aq. solns. of eserine salicylate (A) prepd. with distd.  $\text{H}_2\text{O}$  satd. with  $\text{BzOH}$  remain colorless for at least 4 weeks; solns. without  $\text{BzOH}$  begin to color after 2 days, whether exposed to daylight or kept in the dark. Salicylic and cinnamic acids have the same effect as  $\text{BzOH}$ . Soln. A, of 0.5%, contg.  $\text{BzOH}$  when heated in ampoules to  $100^\circ$  for 30 min., shows a faint color; without  $\text{BzOH}$ , the coloration becomes red. The acidity due to  $\text{BzOH}$  causes no pain in eye treatment. S. WALDBOTT

**Additions to and modifications of the pharmaceutical Codex.** ANON. *J. pharm. chim.* **25**, 411-6(1922).—Copy of the official document, decree of March 30, 1922. S. WALDBOTT

**Identity characters of a distilled cherry-laurel water.** H. PECKER. *J. pharm. chim.* 25, 424-9(1922).—The official prepn. (A) should contain 1 g. of HCN per l., and about 3 g. + of BzH (theory: 3.93 g.) Then the amt. of free HCN will be at most 0.25 g. per l. On adding *Denner's reagent* (for BzH) modified, (PhNHNH<sub>2</sub>, redistd. 1 cc.; glacial AcOH 0.5 cc., H<sub>2</sub>O to make 100 cc.; soln. of NaHSO<sub>3</sub> 20 drops) A forms a ppt. nearly at once, in the cold; solns. of HCN merely dild. with small amts. of A are not at once pptd. De Myttenaëre detects added synthetic BzH (contg. traces of BzOH) with Congo red soln.; 1 drop added to 5 cc. of A produces a garnet-red, in artificial mixts. a bluish color. P.'s *reagent* (NH<sub>4</sub> molybdate 2 g., H<sub>2</sub>SO<sub>4</sub> 5 cc., H<sub>2</sub>O to make 100 cc.) differentiates A from mixts. Five drops added to 5 cc. of soln. of HCN, or BzH, or mixts. of both give no test; but with A a blue color of varying intensity is produced, no doubt caused by a reducing volatile substance. S. WALDBOTT

**Determination of allyl mustard oil in mustard flour.** A. LUCÉ AND A. DOUCET. *J. pharm. chim.* 25, 458-64; *Ann. fals.* 15, 161-6(1922).—In the Codex (Dieterich) method, 6 hrs. maceration causes notable loss of mustard oil formed from the glucoside, due to secondary reaction, also induced by higher temp. During the 1st hr. of maceration, the speed of this decompn. is nil, regardless of temp., (confirming Carles, C. A. 7, 3639), and the hydrolysis of the glucoside is complete. For exact results, leave the AgNO<sub>3</sub>-NH<sub>4</sub>OH soln. in contact with the C<sub>6</sub>H<sub>5</sub>NCS for 1 hr. at 80-85° using reflux; the ppt. is then Ag<sub>2</sub>S (cf. Kuntze, C. A. 2, 1857). With maceration for 1 hr., 5 samples showed 0.99 to 0.87%, one 0.75% of C<sub>6</sub>H<sub>5</sub>NCS; the Codex requires at least 0.70%. S. WALDBOTT

**The preparation of liquid extract of licorice.** PHYLIS QUANTY. *Pharm. J.* 108, 258-9(1922).—The best method is that of the Brit. Pharm. when modified by using maceration with boiling H<sub>2</sub>O, and macerating the marc a third time with 0.5 the amt. of H<sub>2</sub>O used previously. This avoids the formation of a jelly-like liquid difficult to filter after boiling when NH<sub>3</sub> is used in extrn., and the yield is higher than by the Brit. Pharm. method (maceration with CHCl<sub>3</sub>-H<sub>2</sub>O), or by percolation with CHCl<sub>3</sub>-H<sub>2</sub>O or with NH<sub>3</sub>-H<sub>2</sub>O. S. WALDBOTT

**The endocrine organs, and the utilization of their products in pharmacy.** H. DRYERRE. *Pharm. J.* 108, 265-6(1922); *Chemist and Druggist* 96, 418(1922).—An address on the functions of the ductless glands of the body. S. WALDBOTT

**Notes on some Codex formulas.** F. GOLDBY. *Pharm. J.* 108, 147-8(1922).—Improvements are recommended in the prepn. of 11 official articles for adoption in the pending new Codex. S. WALDBOTT

**Cudbear.** ERNEST QUANTY. *Pharm. J.* 108, 280-1, 344, 368(1922); F. GOLDBY. *Ibid* 108, 324, 403.—A soln. of 2-8 g. in 300 cc. of cold H<sub>2</sub>O fades to yellow in direct sunlight in 4 weeks; with CHCl<sub>3</sub> added, or sugar in an amt. as for simple sirup, or if the soln. is boiled and while hot poured into a sterilized bottle, the solns. will keep for more than 3 months. To prep. tincture of cudbear, use pulped filter paper, or brown paper, shredded, washed and made into pulp with boiling H<sub>2</sub>O; remove excess of H<sub>2</sub>O by pressure. Mix cudbear 70 g., with the moist pulp 35 g., in a mortar, then percolate with stronger CHCl<sub>3</sub>-H<sub>2</sub>O to produce 450 cc., add 150 cc. of 90% EtOH. Filter if necessary. G. in reply upholds the advantage of his use of sand (cf. preceding abst.) S. WALDBOTT

**Yohimbe bark, its history and identification in commerce.** J. SMALL AND MISS F. M. J. ADAMS. *Pharm. J.* 108, 266, 282-5, 311-4(1922); *Chemist and Druggist* 96, 418-9(1922).—The detailed medical, botanical and chem. history is given, with literature references appended. The macro- and microscopic characters of the true and the false barks are recorded. The differences may be checked by color tests with dil. NaOH or NH<sub>4</sub>OH. Shake a few scrapings from the inner surface of the secondary



bark with dil. NaOH soln. (10 drops of soln. of d. 1.168 in 30 cc. H<sub>2</sub>O); the genuine bark shows wine-red to reddish brown; the false bark merely brown, with a faint tinge of red. The tests are more distinct, only develop more slowly with NH<sub>4</sub>OH (5 drops of soln., sp. gr. 0.880 in 10 cc. H<sub>2</sub>O). Cf. C. A. 3, 1442. S. WALDBOTT

**Solubility of phenol in liquid paraffin.** J. COFMAN-NICORESTI. *Pharm. J.* 108, 349(1922).—The soly. of PhOH in liquid paraffin at 15° is not above 1%. The amt. of PhOH exceeding 1%, when dissolved in liquid paraffin by heat, will on cooling sep. in an oily layer below the soln. The great danger of prescribing such solns. with more than 1% is pointed out. S. WALDBOTT

**Opium.** A. C. ABRAHAM, H. E. DIGBY AND J. RAE. *Pharm. J.* 108, 353-7 (1922); *Chemist and Druggist* 96, 555-6(1922).—The paper includes the prepn. of tincture, the detn. of morphine, the substances which interfere with its detn. and extn. and the loss of morphine in powder on keeping. As to tincture, the Brit. Pharm. process is considered wasteful and laborious; Redwood's process of 1885 should be reverted to, with the addition of percolation. In the assay of opium, the waxes, etc., interfere with the detn. of morphine; in accurate work they must first be removed and tested for morphine, unless an allowance can be made for them. In sifting, all the opium must pass through the same sieve so as to obtain a representative sample for the detn. Opium in powder loses strength, but liquid preps. do not. Some method should, if possible, be devised to remove enzymes or destroy them in powdered opium before it is used in preps. or otherwise. The details of the proposed prepn. of tinctura opii, and of an improved assay for morphine are given. S. WALDBOTT

**Standards for surgical dressings.** F. BROWNE. *Pharm. J.* 108, 357-9(1922); *Chemist and Druggist* 96, 556-8(1922).—Such standards are included in the new Supplement to the Brit. Pharm. Codex. A review is given, including the definitions and requirements for plaster of Paris bandages, absorbent cotton wool, its mode of manuf., test for absorbency, etc. S. WALDBOTT

**Opium.** P. A. W. SELF. *Pharm. J.* 108, 401, 46(1922); A. C. ABRAHAM. *Ibid* 108, 419, 464-5(1922).—Polemical. S. denies that to insure complete extn. of morphine, previous treatment with a volatile solvent is necessary; simply careful trituration of the opium with the H<sub>2</sub>O and Ca(OH)<sub>2</sub> is essential. S. also denies loss of morphine on keeping of dried opium; weighing the morphine instead of titrating it is a retrograde step, as it may contain Ca salts. A. in rejoinder upholds all his contentions; that of the loss of morphine is supported by Debourdeaux (C. A. 7, 680). S. W.

**Powdered cinnamon bark.** C. T. BENNETT. *Pharm. J.* 108, 424(1922).—In 6 samples powdered before examn., the ash varied from 5.5 to 3.5%; total Et<sub>2</sub>O ext. 2.52-1.36; volatile Et<sub>2</sub>O ext. 1.31-0.66; ext. of 1:5 tincture 1.85-1.45%. In 11 samples of powd. com. bark, the ash varied from 3.5 to 9.9%; in 8 cases it was above the limit set by the Brit. Pharm. Total Et<sub>2</sub>O ext. 3.58-0.94; volatile Et<sub>2</sub>O ext. 1.88-0.20; ext. of 1:5 tincture 1.13-2.05%. The Brit. Pharm. ash limit should be omitted since it does not apply to the powd. bark. A limit for volatile Et<sub>2</sub>O ext. should be introduced. Cf. C. A. 5, 2413. S. WALDBOTT

**Determination of the ash of rhubarb.** J. F. LIVERSEEGE. *Pharm. J.* 108, 426 (1922).—The ash in a given sample of East Indian rhubarb varied from 11.5 to 19.3% while the Brit. Pharm. allows a max. of 15%. The variation is due to the presence of much CaC<sub>2</sub>O<sub>4</sub>, forming CaCO<sub>3</sub> or CaO or a mixt. of both. To obtain uniformity, ash 1 g. of rhubarb at a moderate temp., stir with 25 cc. H<sub>2</sub>O, let stand for 1 hr., add 2 cc. of about 5 N (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> and evap. to dryness on a water-bath. Dry for 30 min. in a water oven and weigh. In the next Brit. Pharm., the mode of detn. of ash should be better defined. S. WALDBOTT

1922

**Pharmacy in California.** F. A. SMITH. *Pharm. J.* 108, 470-1(1922).—A comparison with British practice. The required knowledge of toxicology is an advantage.

S. WALDBOTT

**The production of cacao.** M. RIGOTARD. *Rev. sci.* 1921 (July 23), 407; *J. pharm. chim.* 25, 365-7(1922).—Mode of cultivation and statistics are given, showing lagging production by the French colonies.

S. WALDBOTT

**Essential oils.** ROURE-BERTRAND FILS. *Sci. ind. bull.* [4] No. 4, Oct. 1921; *Grasse* 1921. A detailed botan. study of *Lavandula stoechas* and *L. dentata* by Mlle. A. Camus is given. An oil distd. from *L. stoechas* in 1921 resembled in compn. and character that of Schimmel & Co. (1905), later ascribed by them to *L. dentata* (C. A. 9, 2693). The oil of *L. stoechas* has the const.:  $d_{20}$  0.945-0.962, optical rotation  $+35^{\circ} 30'$  to  $+47^{\circ}$ , acid no. 0.93-5.16, sapon. no. 18.26-18.67, ester no. 13.1-17.74, acetyl ester no. 47.14, soly. in 60% EtOH 5 vols. +. The chief constituents (80%) are *d*-camphor and *d*-fenchone, probably also fenchyl alc., terpineol and a phenol compd. The purified *d*-fenchone had the const.  $d_{20}$  0.9443,  $d_{25}$  0.9402, optical rotation ( $23^{\circ}$ )  $+54^{\circ} 34'$ ,  $n_D^{25}$  1.4625,  $m$ . 3  $5^{\circ}$ . Oil of angelica root, obtained with a yield of 0.4% by distg. the ground fresh root with 15 parts of H<sub>2</sub>O, showed  $d_{20}$  0.8887,  $d_{25}$  (corr.) 0.8907, optical rotation ( $18^{\circ}$ )  $+6^{\circ} 42'$  (normally  $16^{\circ}$  to  $+41^{\circ}$ ), acid no. 7.20 (usually 1 to 4), sapon. no. 52.27 (13 to 44), ester no. 45.07 (12 to 40), soly. in 90% EtOH 2 vols. +. The oil was inferior to that from dry roots. Sep. the H<sub>2</sub>O from the oil and ext. the H<sub>2</sub>O with petroleum ether; a deep red oil is yielded, acid no. 20.53, sapon. no. 134.4, sol. with opalescence in 90% EtOH, clear with 95%. Madagascar cinnamon bark oil was obtained from pounded bark with a yield of only 0.17% (A), but the sepd. H<sub>2</sub>O when extd. with petroleum ether yielded 0.3% (B) of different character. The const. of A, B and C (A + B) were:  $d_{17}$  0.9715, 1.0281, 1.0075;  $d_{20}$  0.9731, 1.0297, 1.0091; optical rotation  $-5^{\circ} 49'$  ( $17^{\circ}$ ),  $-2^{\circ} 2'$  ( $16^{\circ}$ ),  $-3^{\circ} 23'$  ( $17^{\circ}$ ); acid no. 2.49, 2.49, 2.49; aldehyde content 48%, 82%, 70%. A is insol. in 70% EtOH, sol. in 1 vol. 80% EtOH, opalescent up to 10 vols.; B is sol. in 0.75 vol. 70% EtOH and 0.75 vol. 80% EtOH, opalescent. C is sol. in 2 vols. 70% EtOH, opalescent with more EtOH. The oils are inferior to the Ceylon oil. The table of structural formulas, physical const. and characteristic derivs. of essential oil constituents (C. A. 14, 3753) is continued and includes the remaining phenols, and the acids. A monograph on French oil of lavender is given, its distn., compn., analytical characters, methods of assay and detection of adulterants, *e. g.*, foreign esters (cf. C. A. 14, 3497; 16, 1293). Abnormal santalwood oils may be deficient only through incomplete extn. of the wood by distn. (E. J. Parry, *Parfumerie moderne* 3, 54(1921)). "Petrohol" is isopropyl alc. from petroleum by the C. Ellis process (L. Lazennec, *Parfumerie moderne* 6, 112(1921)). Oil of *Tagetes anisala* Lillo, a composite growing in the high prairies of the Argentine Republic, has the odor of anise; the yield is 0.7 to 0.8% of the green plant. Its const. are  $d_{20}$  0.9862,  $b$ .  $214^{\circ}$ - $218^{\circ}$ ,  $f$ . p.  $-6^{\circ}$ ,  $n_D$  1.5432, optical rotation  $-1^{\circ} 10'$ , soly. in 90% EtOH 1:5, sapon. no. 3.1.

S. WALDBOTT

**Eksip.** ANON. *J. Am. Med. Assoc.* 78, 991(1922).—Eksip is sold in the form of tablets by M. Richartz for the treatment of diabetes. The bulk of the tablets consists of MgCO<sub>3</sub> and starch. A small quantity of an unidentified drug was found. It was not detd. whether this was of vegetable or animal origin. Alkaloids, heavy metals and emodin-bearing drugs were absent. The prepn. is not identical with the Eksip (also a diabetic remedy) examd. by Mannich and Kather in 1915 (*Apoth. Ztg.* 30, 240 (1915)). This was a liquid contg. an extractive from an unidentified drug and a considerable quantity of free HCl.

L. E. WARREN

**Leaven's Asthma Prescription.** ANON. *J. Am. Med. Assoc.* 78, 991(1922).—This prepn. is put on the market by the Leaven Drug Company, Rosedale, Kan. An

original specimen of Leaven's Asthma Prescription was examd. The package contained about 4 fl.-oz. of a dark brownish red, sirupy liquid, having a neutral reaction to litmus and an odor suggestive of a mixt. of oils of sassafras and wintergreen. On evapn. of an Et<sub>2</sub>O ext. of the prepn., a distinct odor like oil of spearmint was observed. The prepn. had a harsh, disagreeable, but somewhat sweet taste, resembling that of KI in sirup. Sucrose, K, I, a trace of Fe and an unidentified yellow dye were detected by qual. tests. EtOH, alkaloids, NH<sub>4</sub> salts, heavy metals, emodin-bearing drugs, phosphates, salicylates, Na salts and sulfates were absent. The absence of alkaloids excludes the presence in the prepn. of such drugs as hyoscyamus and the opium derivs., substances sometimes employed in the treatment of asthma. Quant. examn. indicated that the compn. of Leaven's Asthma Preparation is KI 10.9 g., sucrose 55.0 g., Fe trace, H<sub>2</sub>O, flavoring and color to make 100 cc. It is evident from the analysis that a soln. of about 48 grains of KI in a fl.-oz. of simple sirup would have whatever anti-asthmatic properties are possessed by Leaven's Asthma Prescription. L. E. W.

**Queen of Antiseptics.** ANON. *J. Am. Med. Assoc.* 78, 1072(1922).—This prepn. is sold by Mme. Leonard of Aurora, Ill. The contents of a \$2.00 package weighed 79 g. The material was not completely sol. in H<sub>2</sub>O or in EtOH. The portion of the substance sol. in EtOH responded to tests for H<sub>3</sub>BO<sub>3</sub>. This portion contained neither HgCl<sub>2</sub>, salicylic acid, benzoic acid nor quinosol, substances frequently used as antiseptics. Such astringents as FeCl<sub>3</sub> and tannic acid were absent. The part insol. in EtOH gave tests for a Hg compd., Cl and NH<sub>3</sub>. This indicated the presence of ammoniated mercury. Quant. analysis showed H<sub>3</sub>BO<sub>3</sub> 97 and ammoniated mercury 3%. L. E. W.

**Kolor-Bak.** ANON. *J. Am. Med. Assoc.* 78, 1146-7(1922).—Kolor-Bak is sold by the Hygienic Laboratories of Chicago "to restore gray hair to its original color." Analysis: Pb(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>4</sub>·3H<sub>2</sub>O 0.6 g., pptd. S 1.0 g., PbCl<sub>2</sub> 0.16 g., PbO 0.2 g., NaCl 0.6 g., C<sub>2</sub>H<sub>5</sub>(OH)<sub>2</sub> 2.0 g. per 100 cc., EtOH 4.8% by vol. and H<sub>2</sub>O to make 100 cc. The prepn. is stated to be free from AgNO<sub>3</sub>, Hg salts or other ingredients injurious to the hair or scalp. Cases of poisoning from using Pb-contg. hair dyes have been reported.

L. E. WARREN

**Evans' "Cancer Cure."** ANON. *J. Am. Med. Assoc.* 78, 1739-40(1922).—A mixt. of about 16% dried FeSO<sub>4</sub> with 84% of some fat similar to lard. Cost 5 cents. Price of treatment \$100.00.

L. E. WARREN

**A comparison of eastern and western hemlock oils.** D. E. CABLE. *J. Am. Pharm. Assoc.* 10, 170-3(1921).—The chemistry of hemlock oil is far from settled. Five lots of twigs and needles (leaves) of *Tsuga canadensis* from as many eastern states were collected in the summer of 1919-20. The oil is mostly contained in the leaves. The yields of oil from the stripped leaves varied from 0.29 to 0.65%, the largest yield being from leaves collected during the later summer months.  $d_{4}^{20}$  0.9020 to 0.9234;  $n_D^{20}$  1.4691 to 1.4704;  $[\alpha]_D$  -14.80° to 21.65°; acid no. 0.33 to 0.70; ester no. 103.8 to 147.35; ester as bornyl acetate, 36.33 to 51.57%; free borneol 2.16 to 5.89%; total borneol 31.24 to 39.83; substance other than bornyl acetate and free borneol 41.54 to 60.98%. Three specimens of hemlock were obtained from Idaho which had been collected in May, June and July, resp. The yields of oil from the stripped leaves were 0.36, 0.32 and 0.32%;  $d_{4}^{20}$  0.8444, 0.8521 and 0.8490;  $n_D^{20}$  1.4790, 1.4840 and 1.4806;  $[\alpha]_D$  -6.74°, 16.99° and 20.0°; acid no. 2.57, 3.4 and 3.2; ester no. 17.25, 17.2 and 6.7; ester as bornyl acetate 6.04, 6.02 and 2.35%; borneol as ester 4.75, 4.73 and 1.85%; free alc. as bornyl 3.87, 4.51 and 3.58%; total borneol 8.62, 9.24 and 5.43%; other substances 90.09, 89.74 and 94.07%. The consts. for three specimens of com. hemlock oil were  $d_{4}^{20}$  0.9664, 0.9190 and 0.9310;  $n_D^{20}$  1.4796, 1.4721 and 1.4760;  $[\alpha]_D$  -14.13°, -24.85° and -19.92°; acid no. 18.45, 3.59 and 1.51; ester no. 108.05, 115.41 and 1.0509; ester as bornyl acetate 29.71, 31.74 and 28.91%; borneol as ester 29.71, 31.74 and 28.91

%; free alc. as borneol —, 10.0 and 12.64%; total borneol —, 41.74 and 41.55%. Other substances —, 49.61 and 50.58%.

L. E. WARREN

**The relative activity of different parts of the digitalis plant.** GEO. E. ÉWE. *J. Am. Pharm. Assoc.* 10, 362-8 (1921).—One hundred whole green digitalis plants were collected and sepd. into leaves without petioles 54.3%, petioles 34.1%, roots and crowns 6.4% and loss in handling as moisture 5.4%. On drying the drug for grinding the losses were leaves without petioles 74.8, petioles 83.4 and roots and crowns 64.7%. The physiologic activity of the sepd., dried parts was detd. for each fraction and the results were compared with U. S. P. digitalis. Whole plant 166%; leaves without petioles 250%; petioles 118%; roots and crowns 177%. A tincture was prepd. from each of the several dried fractions and the tinctures were assayed for digitoxin. The results are given in terms of g. per 100 cc. Whole plant 0.0145 and 0.0160 g.; leaves without petioles 0.0285 and 0.03009 g.; petioles 0.0105 and 0.01259 g.; roots and crowns 0.0068 and 0.0064 g. The total ash and the acid-insol. ash were detd. for the several parts. Whole plant 32.7 and 25.7%; leaves without petioles 20.8 and 13.6%; petioles 27.7 and 19.5%. The extractive in the tinctures amounted to 1.83 to 1.93 g. per 100 cc. for the whole plant, 2.28 to 2.49 g. for the leaves without petioles, 2.30 g. for the petioles and 1.42 to 1.45 g. for the roots and crowns.

L. E. WARREN

**Oil of Bystropogon Canus.** JULIA WHELAN. *J. Am. Pharm. Assoc.* 11, 337-8 (1922).—The material was collected in Bolivia in June by the Mulford expedition and was distd. in Madison in October. The total oil obtained by steam distn. from 28 lbs. was 39.2 g. or 0.3%. The quantity was too small to allow many tests. Color greenish, somewhat like bergamot oil; odor more like fatty acid esters than menthol;  $d_{20}^{20}$  0.910;  $[\alpha]_D^{20}$  -0.59;  $n_D^{25}$  1.563. Tests for pulegone, menthol, thymol and carvacrol were negative.

L. E. WARREN

**Further observations on acriflavine and proflavine.** L. E. WARREN. *Repts. Lab. Am. Med. Assoc.* 14, 58-9 (1921).—Since the first examn. of these products was reported (*C. A.* 14, 3122) other specimens of acriflavine (*A*) and of proflavine (*B*) have been examd. The detns. made were loss at 100°, insol. in  $H_2O$ , ash and Cl (in acriflavine) in the order named. *A* Heyl 4.82 to 5.01, negligible to 0.6; 0.47 to 1.46 and Cl 25.61%; *A* Abbott 6.34, 0.05, 0.017 and 22.07%; *A* Van Dyk 10.93 to 20.52, 0.23 to 1.46, 0.36 to 1.11 and 22.26%; *A* Boots Cl 22.46%. The amt. of Cl found indicates that the molecule of *A* contains 2 Cl instead of Cl as formerly supposed. *B* Heyl 0.12 to 4.24, 0.84 to 1.97, and 0.14 to 0.85%. *B* Abbott 7.32, 0.38 and 0.33%; *B* Van Dyk 2.19 to 5.67, 2.10 to 6.87 and 0.34 to 0.48%. The N. N. R. standards are, resp., not over 10, not over 1 and not over 1%.

L. E. WARREN

**Potassium mercuric iodide.** P. N. LRECH. *Repts. Lab. Am. Med. Assoc.* 14, 59-65 (1921).—Theoretically  $HgI_2$  dissolves in a soln. contg. 2KI, but in practice an excess of KI is required.  $K_2HgI_4$  is sol. in a very small amt. of  $H_2O$ , but on diln. dissociation takes place and some  $HgI_2$  is pptd. Two specimens sold as germicides were examd. Loss at 120°. Merck 2.88; P. W. R. 3.40%. K was detd. by heating with  $H_2SO_4$  and weighing as  $K_2SO_4$ . Merck 9.91; P. W. R. 9.52%. I was detd. by titration with 0.1N  $KIO_3$ . Merck 61.8; P. W. R. 61.7%. *Hg* was detd. by the following method: Dissolve about 2.5 g. of  $K_2HgI_4$  in 10 cc. of  $H_2O$ , and add sufficient KI soln. to prevent pptn. of  $HgI_2$ . Introduce the solution and washings into a cathode cup, previously weighed with its metallic Hg, and add 10 cc. of 20% NaOH soln. Pass an elec. current through the soln., gradually increasing the current so that at the end of 8 min. it will be 2 to 3 amp. and 7 to 10 volts, stirring the soln. by rotating the anode about 500 r. p. m. After 40 min., wash with  $H_2O$ , with the aid of a siphon and without interrupting the current until the current drops to 0. Remove the cathode cup and allow it to stand with 20 cc. of 3% acetic acid until bubbles cease to be evolved. Wash the Hg with  $H_2O$

and EtOH, remove most of the excess EtOH by filter paper, dry in a desiccator over KOH sticks and a beaker of Hg. The Hg content of  $K_2HgI_4$ , calcd. to the dry salt, is not less than 25.0% or more than 26.0%.  
L. E. WARREN

**Some notes on methylatropine bromide.** L. E. WARREN. *Repts. Lab. Am. Med. Assoc.* **14**, 65-7(1921).—Methylatropine nitrate and bromide have been known for some years. The nitrate was sold under the German name eumydrin while the bromide sold under the English name mydrasine. During the war both salts became unobtainable. An American firm now makes the bromide; a specimen of this was examd. The reactions of the product were compared with those of atropine, homatropine, hyoscyamine, scopolamine and eucatropine salts. A white, cryst. powder, permanent in air; lost no wt. over  $H_2SO_4$ . Sol. in  $H_2O$  and EtOH; almost insol. in  $Et_2O$  and  $CHCl_3$ ; aq. soln. clear, colorless, neutral to litmus. Soln. pptd. by most alkaloidal reagents, but not by  $PtCl_4$  or by picric acid; pptd. by  $PdCl_2$ , thus differing from the other mydratics tested; white, curdy ppt. with  $HgCl_2$ ; homatropine gave a white ppt. but not so curdy. It responded to Vitali's test; m. p. 222-3°. Ash unappreciable. L. E. WARREN

#### Action of ergotin on the isolated uterus (Cnrò) 11H.

BEYROUT, G.: **Uroformine au point de vue chimique, physiologique et pharmaceutique.** Paris: Vigot frères. 80 pp. Fr. 6.

BUCHHEISTER, G. A.: **Handbuch der Drogistenpraxis.** 2 Vol. 9th Ed. Berlin: Julius Springer. M 92, bound. Reviewed in *Z. deut. Öl und Fett-Ind.* **42**, 190(1922).

MAHIEU, J.: **Essai bactériologique et chimique des préparations pharmaceutiques dites ferments lactiques.** Paris: Vigot frères. 66 pp. Fr. 6.

**Useful Drugs.** 5th Ed. Chicago: American Medical Association. 80 pp. Fr. 6. Cf. *C. A.* **15**, 2339.

**Complex silver salts of  $\alpha$ -amino acids.** M. GUGGENHEIM. U. S. 1,417,167, May 23. An aq. soln. of glycine on treatment with freshly pptd. Ag oxide, heating, cooling on a freezing mixt. and stirring yields a colorless salt in the form of plates which may be purified by recrystn. from  $H_2O$  contg. glycine. The compd. is somewhat sol. in  $H_2O$  and more sol. in the presence of glycine or other  $\alpha$ -amino acids. The aq. soln. is alk.  $AgNO_3$  soln. boiled down *in vacuo* with glycine yields a cryst. mass.  $Ag_2SO_4$  finely ground with glycine yields a product more sol. than  $Ag_2SO_4$ . The Ag salt of alanine is prepd. by pulverizing alanine with an equiv. of freshly pptd.  $Ag_2O$ . Ag carbamide ground with glycine yields a product slightly sol. in  $H_2O$ .  $AgOAc$  and glycine give a product about 5 times as sol. in  $H_2O$  as  $AgOAc$ . Ag salicylate and glycine also give a sol. product. Other  $\alpha$ -amino acids may be combined with Ag to form complex salts but aromatic amino acids and betaines do not give similar reactions. Aq. solns. of these products are stable even when heated and do not yield a ppt. with NaOH or  $Na_2CO_3$  nor do they ppt. albumin. Because of their stability and the fact that they are not irritating to the mucous membrane they are adapted for use as therapeutic agents.

### 18—ACIDS, ALKALIES, SALTS AND SUNDRIES

FRED C. ZEISBERG

**The composition of commercial phosphoric acid.** WILLIAM H. ROSS, C. B. DUGGIN AND R. M. JONES. *J. Ind. Eng. Chem.* **14**, 533-5(1922).—Tabulated results are given showing the compn. of different samples of com.  $H_3PO_4$  prepd. from bones and from phosphate rock by the  $H_2SO_4$  method, and from phosphate rock by the volatilization method. The volatilized acids are relatively low in such non-volatile constituents

as Ca, Fe, Al and Mn. The presence of other elements such as Pb, S, Cl and F in unrefined acids depends more on contamination and on the compn. of the rock or bones from which they are obtained than on the process used in their prepn. The lowest proportion of inorg. constituents in the samples analyzed was found in a volatilized acid that had been collected in a Cottrell precipitator and commercially refined. An outline is given of the methods used in making the analyses. W. H. ROSS

**Elimination of the heat of reaction in the synthesis of ammonia by superpressures.** GEORGES CLAUDE. *Compt. rend.* **174**, 681-3(1922).—The heat is used to warm the fresh gas to the reaction temp., and this is done immediately around the catalyzer tube. The heavy steel inclosing tube is thus protected from temp. gradients which, in view of the high pressure, would cause many failures. Cf. C. A. **15**, 576, 1377. W. P. W.

**An alleged synthesis of ammonia.** A. J. PRINCE. *Chem. News* **124**, 256-7(1922).—German pat. 74,275, "A process for the synthetic preparation of ammonia," based on the reaction  $N_2 + 3H_2 + 2CO + 2H_2O = 2HCOONH_4$  in presence of a catalyst, is shown not to yield even a trace of  $HCOONH_4$  with platinized asbestos as catalyst. The process is useless, but is often quoted in the literature. E. G. R. ARDAGH

**Hydrogen as a byproduct of synthetic soda and ammonia.** UMBERTO POMILIO. *Giorn. chim. ind. applicata* **4**, 56-9(1921).—A description of the processes employed, with sketches of the app. used. ROBERT S. POSMONTIER

**Phosphate ores.** PIETRKOWSKI. *Naturwissenschaften* **10**, 350-1(1922).—P. does not agree with Goldschmidt that the natural supplies of phosphates are limited to a period not much over a century (cf. *Naturwissenschaften* **9**, 887(1921)). In Morocco alone are available over 1,000,000,000 tons not included by Goldschmidt (cf. *American Fertilizer* **53**, No. 8(1920)), as well as large deposits in Tunis, Algiers and Egypt. C. C. DAVIS

**Phosphates.** V. M. GOLDSCHMIDT. *Naturwissenschaften* **10**, 351(1922).—In reply to Pietrkowski (see preceding abstract) G. considers the reserve supplies mentioned by P. too uncertain and of a quality low enough to preclude their exploitation and utilization by present methods. C. C. DAVIS

**The work of the experimental kelp-potash plant of the Bureau of Soils.** J. W. TURRENTINE. *Chem. Age (N. Y.)* **30**, 224-5(1922).—The exptl. plant at Summerland, Cal. succeeded in working up a profitable process for making "kelpchar" (decolorizing C) from kelp, with potash and iodine as by-products. The plant has been sold to a private producing company. F. C. Z.

**Hydrogen peroxide—a novel process for its manufacture.** H. A. DOERNER. *Chem. Met. Eng.* **26**, 1111-2(1922).— $BaO_2$  added slowly in a cold water suspension to a soln. of  $CO_2$  under pressure produces fair yields of  $H_2O_2$ . A unit was built which consisted of: a 6 ft.  $\times$  6 ft. vertical cylindrical iron tank with a mech. stirrer, a false bottom of canvas filter-cloth supported by a wooden frame and an outlet pipe with valve below the false bottom. Valve-controlled inlets for compressed air,  $CO_2$ , and  $BaO_2$  suspension and a pressure gage, small outlet cock for sampling, and a thermometer well were also provided. Best results were obtained at about 0.2 N acidity and under these conditions  $BaCO_3$  formed was granular, but flocculent when high acidity or alkalinity existed. Av. yields of but 80-5% were due to faulty mech. and thermal control. After filtering the charge, the  $BaCO_3$  was washed with water and the washings were used as an initial soln. for the next run. Slow filtering lowered the yield. Ba held in soln. as bicarbonate is partially pptd. with  $H_2SO_4$  and final traces with  $H_3PO_4$ . After refiltering, the  $H_2O_2$  soln. was run to storage tanks and air bubbled through it to remove  $CO_2$ . Causes for instability of the soln. are undetd. for impurities, present in the product of the old processes and derived from the acid used, are missing in the product of this method. W. H. BOYNTON

**Commercial preparation and use of fuller's earth.** T. POOLB MAYNARD AND L. E. MALLON. *Chem. Met. Eng.* 26, 1074-6(1922).—The commercial use of fullers earth is based upon its bleaching power. U. S. earths have been found possessing greater bleaching power than the English earths, but at the same time having an excess oil retention, due to lack of proper grinding and technical control. The possible value of an undeveloped earth depends upon a geological interpretation of its origin, the chem. analysis of hydrous  $\text{SiO}_2$  and Al silicates (which have a value in predicting bleaching quality), the location with respect to transportation, the inherent superior qualities of the earth, the prepn. that develops these qualities, and the technical control of the product. Fullers earth adsorbs basic dyes, offering a possible widened market for it in cheap "clay pigments" while the property of adsorbing bases gives it a value as a water softener. Increased markets and values demand emphasis on the technical control of its production.

W. H. BOYNTON

**The Devillers process for the extraction of iodine from seaweed.** L. LAPICQUE. *Bull. officiel direction recherches sci. ind. inventions* No. 31, 284-6(May 1922).—The I is nearly all removed by washing the seaweed in such a manner as not to remove the hydrocarbons. It behaves as though it were combined as an iodide, and is present in the wash water to the extent of 0.1%. It is pptd. as  $\text{Cu}_2\text{I}_2$  in appreciably acid soln., by adding  $\text{Cu}_2\text{Cl}_2$  with const. stirring. Enough  $\text{SO}_2$  must be added to combine with any O in the soln. The ppt. is agglomerated by means of gelatin or tannin. It is easily sepd. and dried and then contains 50-75% of I by wt. It is worked up for I or for KI by known methods. Several hundred kg. of the  $\text{Cu}_2\text{I}_2$  have been prepd. The merits of the process are: practically no loss of I (at least 33% is lost by burning the seaweed), the org. matter can be used for fodder or for fertilizers, the  $\text{Cu}_2\text{I}_2$  is easier and cheaper to work up than the kelp.

A. P.-C.

**A graphic representation of the rate of conversion in the Deacon process.** BERNHARD NEUMANN. *Z. angew. Chem.* 35, 130-2(1922).—The first systematic exptl. investigation was made by Lunge and Marmier (*Z. angew. Chem.* 1897, 105) when they endeavored to establish a decompn. gradient for gas mixts. of varying proportions of HCl and  $\text{O}_2$  by passing over  $\text{CuCl}_2$  between the temps. of 430° and 550°. Lewis (*C. A.* 1, 5) established equil. conditions for static gas mixts. at 352°, 386° and 419° using  $\text{CuCl}_2$ . V. v. Falkenstein (*C. A.* 3, 854) investigated the reaction at 450° with  $\text{CuCl}_2$ , and at 600° and 650° with  $\text{PtCl}_4$ . F. expressed the equil. const. as  $\log K = (5750/T) - 2.136 \log T - 0.000857T + 0.633 \times 10^{-7} T^2 + 0.296$ . Treadwell (*Z. Elektrochem.* 23, 177(1917)) simplified this to  $\log K_p = (6034/T) - 6.972$  which gives the ratio from room temp. to 1800°. Neumann and Preuschen (*C. A.* 9, 2429) investigated the rate of conversion using  $\text{CuCl}_2 \cdot 2\text{NaCl}$  at a temp. between 410° and 510°. It is not practical to operate below 400° and since the value of  $\log K_p$  becomes negative at 600° the optimum operating condition lies somewhere between. To understand more thoroughly the most favorable conditions all data available were tabulated and plotted as follows: (1) Comparison of values of  $\log K_p$  from the formula of Treadwell and those obtained by other investigators; (2) decompn. rate in gas mixts. of 25% HCl and 75% air at various temp.; (3) decompn. rate with varying HCl concn.; and (4) equil. const. at various temps. for gas mixts. with 25% HCl and 75% air. All the results show the same course of first increasing to a max. at 470° and then decreasing regularly. Using  $\text{CuCl}_2$  as the catalyst the equil. lies between 430° and 450° while with  $\text{CuCl}_2 \cdot 2\text{NaCl}$  this value is raised to 470°. The effect of varying amts. of  $\text{H}_2\text{O}$  vapor is noted and plotted. The presence of moisture lowers the conversion to a marked degree.

A. L. D.

**New uses for zirconium.** R. E. KIRCHNER. *Chem. Ztg.* 46, 380(1922).—Large deposits of zircon in South America and Mexico make this substance of potential importance. It has been used as an abrasive, in making "siloxyl" glass (superior to quartz

glass because not sensitive to the action of oxides of the heavy metals), etc.  $ZrO_2$  is the best elec. insulator at high temps., e. g.,  $2000^\circ$ . It can be used for making refractories, enamels, coloring porcelain dark violet, prepg. high-grade steels, and jackets for electric furnaces. Zr can be employed as a substitute for Pt for many purposes, especially in chem. labs. Its carbide might replace the diamond for cutting tools in the glass industry.

W. C. EBAUGH

**Synthetic mother-of-pearl.** CLEMENT AND RIVIÈRE. *Compt. rend.* **174**, 1353-6 (1922).—A method of pptg.  $CaCO_3$  in an albuminous medium, in the form of a diffraction grating which gives a physical structure resembling mother-of-pearl and the same property of iridescence.

C. R. PARK

**The manufacture of shoe polishes.** MAURICE DE KEGHEL. *Rev. prod. chim.* **25**, 253-60, 293-6 (1922).—A description of the various shoe polishes having a wax base, their methods of manuf. and merits.

A. P.-C.

Catalysts and chemical equilibrium [Deacon's process] (CLARENS) **2**,

HACKSPILL, LOUIS: *L'azote*. Paris: Masson et Cie. 284 pp. Fr. 14.

URBAIN, EDOUARD: *Recherches sur la fixation de l'azote a l'etat de cyanure*. Paris: J. Hermann. 261 pp. Fr. 15, bound Fr. 18.

**Synthesis of ammonia.** I. W. CRIDERBERG. *Can.* **219**, 825, June 20, 1922. A catalyst for  $NH_3$  production contains a complex Fe cyanide of an alkali metal, in which the proportion of alkali metal cyanide to Fe cyanide is less than 2 to 1. The catalyst is heated to a temp. below  $500^\circ$  in an inert atm. and then in a H-N mixt. at a temp. below  $400^\circ$ . Cf. *C. A.* **16**, 617.

**Ammonium chloride.** N. T. BACON. U. S. 1,416,772, May 23.  $NH_4Cl$  is recovered from soln. by evapg. the latter in the presence of free  $NH_3$  which prevents corrosion of the app. from dissociation of the  $NH_4Cl$ .

**Sodium carbonate sulfate from natural brines.** G. B. BURNHAM. U. S. 1,417,139, May 23. Searles Lake brine or a similar brine is evapd. slowly to produce satn. with Na carbonate sulfate, which is crystd. out on further slow evapn.

**Arsenical compounds.** K. B. EDWARDS. *Can.* **219**, 170, May 30, 1922. In the production of salts of the general formula  $RAsS_4$ ,  $As_2S_3$  is treated with an alkali monosulfide and alc. is added to aid the pptn. of the salts. Cf. *C. A.* **15**, 3183.

**Oxidizing phosphorus.** I. HECHENBLEIKNER. *Can.* **219**, 466, June 6, 1922. A mixt. of phosphatic material, a flux and carbonaceous material is heated in a furnace. A mass of the phosphatic material and flux is conducted to the furnace, and is preheated by the passage therethrough of the gases from the furnace, while the C is separately fed into the furnace and air or O is introduced into the stream to oxidize the P and CO to  $P_2O_5$  and  $CO_2$  resp. App. is also specified.

**Enriching gases in sulfur dioxide.** G. C. HOWARD. U. S. 1,417,066, May 23. Smelter gases or the like of low  $SO_2$  content are mixed with additional  $SO_2$  released from an aq. soln. U. S. 1,417,067 relates to counter-current treatment of sulfurous gases and  $SO_2$  soln. in order to recover  $SO_2$  from smelter gases.

**Sulfur from sulfur dioxide.** G. C. HOWARD. U. S. 1,417,068, May 23. *Can.* **219**, 617, May 13, 1922.  $SO_2$  is vaporized from liquid  $SO_2$ , mixed with refrigerated air, and the mixt. is heated and passed over incandescent coke to produce S, which is afterward condensed.

**Sulfur burners.** A. G. HINZKE. *Can.* **218**, 359, May 9, 1922.

**"Plumber's soil."** J. F. LEDDY. U. S. 1,417,258, May 23. A mixt. of ivory black, chalk, cylinder oil, molasses, vinegar,  $H_2SO_4$ , Fe sulfate, gum arabic and  $H_2O$ .



**Refining crude lampblack.** C. F. C. HERTING. U. S. 1,416,955, May 23. Crude lampblack is boiled in a dil. soln. of soap and NaOH and then heated with  $H_2SO_4$  to form a paste and the latter is added to  $H_2O$  and treated with a salt soln.

**Fire-extinguishing liquid.** E. R. BRODRON. Can. 219,849, June 20, 1922. A fire-extinguishing compd. contains  $NaHCO_3$  and an  $NH_4$  salt which depresses the freezing point. It may also contain  $Na_2CO_3$ .

**Heating cartridge.** D. LACOUR and C. V. SCHOU. U. S. 1,417,075, May 23. A cartridge of combustible material such as Mg or Al and Fe oxide is provided with an inserted igniting mixt. composed of Mg and Cu oxide to facilitate ignition of the main charge.

**Brake- or clutch-lining.** J. H. SARIS. U. S. 1,416,979, May 23. A compn. of cork and fibrous material is treated with a binder which is resistant to heat and oil, e. g., blood albumin.

### 19—GLASS, CLAY PRODUCTS, REFRACTORIES AND ENAMELED METALS

G. E. BARTON, C. H. KERR

**Manufacture of reflecting telescope disks.** D. E. SHARP AND W. H. RISING. *J. Ind. Eng. Chem.* **14**, 511-5(1922).—Reflecting telescope disks may be made by casting molten glass into a suitable mold, and annealing in an elec. or a gas-fired furnace. Special equipment is required for obtaining the slow cooling rates. An important innovation is the use of a low-expansion glass for minimizing change of figure in the finished mirror due to temp. change.

D. E. S.

**Mechanical tests for raw materials used in the manufacture of porcelain.** W. DEMUTH. *Elektrotechn. Z.* **43**, 605-610(1922); 15 illus.—A detailed description of the new Hermsdorf lab. and equipment.

C. G. F.

**Possible utilization of some sands of Montescaglioso (Potenza).** LUIGI PARLATI. *Giorn. chim. ind. applicata* **4**, 13-5(1921).—Four samples of sand from different localities were analyzed with the following results, respectively, for Red sand (A), Gravina Rapids sand (B), Bradano River sand (C) and Lella Road sand (D): Sp. gr. 2.40, 2.75, 2.45, 2.29; loss at  $100^\circ$  2.36, 0.50, 0.63, 1.01%;  $CO_2$ , —, 10.26, 7.07, 5.19; loss at red heat 2.83, 11.90, 9.21, 6.60; total  $SiO_2$  81.50, 63.85, 70.56, 73.87;  $Al_2O_3$  8.56, 4.71, 6.01, 5.21;  $Fe_2O_3$  3.41, 2.13, 0.93, 3.29; CaO 1.01, 15.18, 11.13, 8.80;  $K_2O$  1.90, 1.06, 0.64, 1.70;  $Na_2O$  1.74, 2.05, 2.24, 0.41; total 100.95, 100.88, 100.72, 99.88. A is brownish red of not very fine grain, contg. about 58% quartz and 29 feldspar. B is rather coarse, of dull color, and contains 3.38% clay, 47 quartz and 21 feldspar. C is brownish and of fine grain, contg. 2% clay, 51 quartz and 24 feldspar. D is white very fine-grained and contains 1.47% clay, 58 quartz and 28 feldspar. The sands may be utilized (1) in agriculture, to correct compact soils by improving their capacity for water, air and heat, capillary action and hygroscopicity, and increasing the content in  $SiO_2$ ; (2) in the ceramic industry, to mix with clays as antiplastic cements; (3) in the prepn. of mortars and building materials; (4) in glass making, especially for very fusible glass and glass having properties of great inalterability, devitrifying very slowly under changes of temp., also for bottle glass. In using the sands for glass making, Na and K compds. must of course be added to make up for the deficiency in these elements present in the sands.

ROBERT S. POSMONTIER

**Aging of ground clinker.** LE GUEN. *Rev. Mat. Constr. Trav. Pub.* **151**, 76(1922).—Clinker, sepd. from CaO by bolting, is ground in ball mills to 60-mesh and then stored for aging. The grinding cuts down the aging period 80%. A more homogeneous product is also insured.

LOUIS NAVIAS

**Kilns for tiles.** A. E. BUCH. *Kalk, Gips u. Schamotte-Ztg.* **28**, July 21, 1921; *Chimie et industrie* **7**, 941(1922); cf. *C. A.* **16**, 1843.—A discussion of the various factors influencing the choice of kiln, together with a description of various types of kilns and their respective merits. A. P.-C.

**Lighting up a modern vertical cement kiln.** C. TSOUNTAS. *Rev. Mat. Constr. Trav. Pub.* **151**, 70-1(1922). LOUIS NAVIAS

**Absorption of hollow tile.** *Technical News Bulletin of U. S. Bureau of Standards* **60**, 12(1922).—Various methods are compared. Specimens were immersed in cold  $H_2O$  for periods up to 9 days and in boiling  $H_2O$  for periods up to 5 hrs. Similar detns. were made under vacuum and finally the total porosity was obtained by vol. and sp. gr. measurements. The results are, in general: (1) Absorption detd. by cold  $H_2O$  immersion is not complete enough to give practical and consistent results. (2) The best practical method consists in boiling for 5 hrs., cooling to room temp., and soaking for 1 hr. (3) Proper treatment under vacuum will give nearly full satn. and porosity, but the method is probably too complicated for general use. H. F. S.

New uses for zirconium (KIRCHNER) **18**. Refractory materials [for the gas industry] (FULWEILER) **21**. Clays as dispersed systems (ODEN) **2**.

**Refractory material.** WM. A. FRANCE. *Can.* **219,609**, June 13, 1922. A small amt. of molten  $MgCl_2$  is mixed with burned magnesite, the mixt. is moistened, then molded and pressed into the desired shape and allowed to dry without burning.

**Abrasive and refractory articles.** A. H. ANDERSON. *Can.* **219,646**, June 13, 1922. A compn. for forming ceramic articles contains refractory or abrasive cryst. grains, a plastic clay, water and an oily lubricating agent. Cf. *C. A.* **15**, 740.

## 20—CEMENT AND OTHER BUILDING MATERIALS

C. N. WILEY

**The destruction of cement by water and waste waters.** A. SPLITTGERBER. *Wasser* **17**, 87-9(1921); *Chimie et industrie* **7**, 942(1922); cf. *C. A.* **15**, 4044.— $CaSO_4$  contained in water reacts with the  $CaO$  and  $Al_2O_3$  of the cement forming crystals of  $Al_2O_3 \cdot 3CaO \cdot SO_4 \cdot 30H_2O$ , and sulfates of  $Ca$  and  $Al$ . The effects of free acid are of secondary importance.  $Ca(HCO_3)_2$  can react according to the equation  $Ca(HCO_3)_2 + CaO = 2CaCO_3 + H_2O$ . S. mentions various precautions to be taken with respect to the disposal of industrial wastes, and for the prevention of the penetration of these wastes into concrete: (a) use of special cements, e. g., slag cements; (b) addn. of such substances as trass, hydraulic lime,  $BaCO_3$ , water glass, etc., which protect the cement by their chem. action; (c) addn. of substances such as soaps, oils, fats, etc., which act mechanically. Exposed surfaces should be protected by a coat of tar, asphalt, etc.

A. P.-C.

**The behavior of cements in calcium sulfate solutions.** STREBEL. *Zement* **10**, 385-6, 397-8, 409-11, 421-3(1921); *Chimie et industrie* **7**, 942-3(1922).—Since the work of LeChatelier, Candlot, and Michaelis (1880-1890) there has been no appreciable progress in our knowledge of the reactions of sea water on cement. S. gives an account of his work, and advanced theories which he has evolved as a result, with the hope that they will be discussed and may help in definitely solving the problem. The expansion phenomena in cement are due to the formation of large quantities of crystals having a greater vol. than the original compds. present in the cement, which crystals can be formed

only in supersatd. solns. The disappearance of a large proportion of the CaO must be due to its dissolving out, as proved by the formation, on test pieces, of large amts. of  $\text{CaCO}_3$  crystals due to the action of atm.  $\text{CO}_2$ . S. claims that CaO is much more sol. in satd.  $\text{CaSO}_4$  solns. than in distd. water, which is not in contradiction with the ionic theory if one admits the formation of a basic sulfate of Ca which is ultimately transformed into carbonate by atm.  $\text{CO}_2$ . The  $\text{SiO}_2$  content of the cement also comes into play. As shown by Candlot, during hardening the hydrated Ca aluminate is transformed by  $\text{CaSO}_4$  into a Ca sulfoaluminate having the formula  $2(\text{Al}_2\text{O}_3, 3\text{CaO}) + 5\text{CaSO}_4$ , according to Candlot and Michaelis. This compd. is quite sol. and gives large crystals which Michaelis has called "Cement bacilli." The formation of this compd. is limited by the action of " $\text{SiO}_2$  which is capable of producing this reaction," referring indirectly to Fe and slag cements which do not readily form this compd. It is also limited by the  $\text{Ca}(\text{OH})_2$  content of the cement. The  $\text{CaSO}_4$  soln. exerts its influence in the voids of the cement during hardening. If there are sufficient voids to lodge the crystals which are formed, the concrete is not deformed; otherwise it expands. A. P.-C.

**Influence of calcium chloride on the tensile and crushing strength of portland cement.** C. R. PLATZMANN. *Zement* 10, 499-502(1921); *Chimie et industrie* 7, 943 (1922).—P. describes expts., which he undertook, to find the reason of the increase in strength and decrease in contraction caused by  $\text{CaCl}_2$  in the manuf. of artificial stones. He attributes this action mainly to hygroscopicity of the  $\text{CaCl}_2$  which, by absorption of moisture during the first few weeks, prevents the shrinking and cracking of the cement, and protects it from too rapid a loss of moisture, thus increasing the strength at the end of 28 days. The subsequent decrease in strength is due to the harmful action of the  $\text{CaCl}_2$ , which P. thinks can even cause expansion. He also thinks that an increase in the setting temp. facilitates crystn. The work is being continued. A. P.-C.

**Influence of the fineness of grinding on the crushing strength of cement.** KILLIG. *Zement* 10, 433-5, 446-8(1921); *Chimie et industrie* 7, 943(1922).—The quality of cement depends mainly on the raw materials and method of burning, so that it is useless to attempt to derive any general relationship, for a given kind of cement, between the fineness and the strength. K. mentions that with a given cement with residues of 1.6-22% on a 900-mesh (presumably per cm.<sup>2</sup>) sieve, the crushing strength, for max. residue at the end of 7 and 28 days, resp., were 224 and 315 kg., and for min. residue were 380 and 525 kg., resp. A. P.-C.

**Artificial stones.** ANON. *Gewerbeblatt* 100, 326-30(1921); *Chimie et industrie* 7, 944(1922).—The applications of magnesian (Sorel) cements are continually increasing on account of the great hardness and beautiful white color of the products made from them. Unfortunately, owing to premature setting in contact with moist air, they cannot be stored for any length of time or shipped. This drawback can be overcome by mixing  $\text{BaCl}_2$  with the  $\text{MgCl}_2$ , and adding enough  $\text{MgSO}_4$ ; so that in the presence of moisture the  $\text{BaCl}_2$  and  $\text{MgSO}_4$  yield Mg oxychloride and finally pure  $\text{MgO}$ . The resulting cement is still of a fine white color and can set with a suitable amt. of aggregate. The author describes various processes for obtaining fine imitation marbles by using metal chlorides mixed with  $\text{MgCl}_2$  instead of colored metal oxides. Similarly, natural stones can be given a mottled appearance by injections in the capillary fissures of the rock. A. P.-C.

**Artificial asphalt prepared from resin as a road binder.** GEORGES DUPONT. *Bull. officiel direction recherches sci. ind. inventions*, No. 31, 310-2 (May 1922). At the time of the high price of tar, a cheaper substitute was sought, more particularly for application to roads. The following substitutes were found useful. (1) "*Pulborite 1*," consisting of a soln. of black pitch in a cheap heavy solvent. The viscous product thus obtained is similar to "tarvia" in appearance and properties; when applied to roads it rapidly pene-

trates to a depth of several cm. and forms an adherent crust. (2) "*Pulvorite 2*," consisting of a soln. of heavy oil in a resin soap paste. It is a black unctuous liquid, miscible with water in all proportions, which can be applied in the form of very dil. soln. When thus applied, atm.  $\text{CO}_2$  decomposes the soap, forming a very hard coating similar to that obtained with (1). (3) "*White pulvorite*," similar to (2) except that the heavy oil is replaced by rosin oil, and having the same properties. Its soln. is white and gives an extremely stable emulsion, showing no signs of sepn. after 6 months. (1) and (2) were tested out on the Bordeaux-Paris road, and gave results similar to what could have been expected from an ordinary treatment with tar, (1) being somewhat better than (2). The cost of these preps. is now higher than that of tar; but they possess the following advantages: easily applied cold, odorless, can be used in repairing roads by applying when building up the roadway, "pulvorite" dust is innocuous to trees. Further uses for them are suggested, such as application to alleys in parks, tennis courts, athletic fields, cellars, stables, and for application on the ground under houses having no cellars.

A. P.-C.

**Improved continuous-operation pot lime kiln.** C. L. NORTH. *Rock Products* 25, No. 3, 47-8(1922).—Mostly mechanical. The main point of interest is in the use of a cone-shaped interior of the kiln rather than the usual kiln constructed with Dutch ovens on two or more sides. A diagram and the advantages of this cone-shaped kiln are given in detail.

E. F. PERKINS

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Possible utilization of some sands of Montescaglioso (PARLATI) 19.

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FABER, OSCAR: **Reinforced Concrete Simply Explained.** London: Frowde, Hodder and Stoughton. 77 pp. 5s.

GARY, MAX: **Versuche über das Verhalten von Mörtel und Beton im Moor.** Berlin: W. Ernst & Sohn. M 84.

TWELVETREES, W. NOBLE: **Concrete and Reinforced Concrete.** London: I. Pitman & Sons. 147 pp. 3s.

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**Cement mixture for coating walls.** L. N. BROWER and P. WERLE. U. S. 1,416,684, May 23. Brixment cement 1090, portland cement 535, lime 185, sand 185, hair 5 and alum 0.5 parts.

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## 21—FUELS, GAS, TAR AND COKE

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A. C. FIELDNER

**The behavior of sulfur in coal during dry distillation.** F. FOERSTER and W. GEISLER. *Z. angew. Chem.* 35, 193-8(1922); cf. *C. A.* 15, 306.—A typical gas coal and several lignites were studied. Detns. were made of pyritic, sulfate, sulfide, and org. S in the coals and the cokes formed from them, and the S in the gas. With coal, the  $\text{H}_2\text{S}$  evolved comes mostly from the pyrite, very little from the org. S. The  $\text{FeS}_2$  decomposes to form  $\text{FeS}$  and S, and these latter form  $\text{H}_2\text{S}$  with the  $\text{H}_2$  and  $\text{H}_2\text{O}$  in the gas. The slight transformation of inorg. to org. S occurs probably through the medium of the  $\text{H}_2\text{S}$ . Lignites contain a larger ratio of org. S to pyrite than do older coals. This org. S is more easily decompd. by heat, and hence lignites evolve more  $\text{H}_2\text{S}$  than do older coals. Lime in the coal ash makes possible the burning of cokes contg. up to 2.5% S without evolution of  $\text{SO}_2$ .

ERNEST W. THIELE

**Inorganic constituents of coal with special reference to Lancashire seams.** II.

**Iron in coal.** F. S. SINNATT AND N. SIMPSON. *J. Soc. Chem. Ind.* **41**, 164-7T(1922).—The work to date on the Fe content of British coals is summarized in 9 tables of analytical data. Pyrite was found pure in some coals but contaminated with considerable Ca and Fe carbonates in other coals. The percentage of Fe extd. by water from 7 different coals varied from 0 to 24.79% of the iron present. As a rule the amt. of Fe extd. by water is small, in some cases the ext. was acid in reaction. From 0.84% to 35.76% of the Fe present went into soln. with 10% HCl. One hours' extn. with HCl removed from the coal all the Fe sol. in HCl. Extn. for 24 hrs. with boiling HCl removed slightly more Fe than 120 hours' extn. with cold acid. Results indicated that HCl-sol. Fe was present in coal in at least 2 forms, ankeritic Fe and  $\text{FeCO}_3$ , both of which may be associated with pyrites. Treatment with  $\text{HNO}_3$  confirmed previous work on American coals (Powell, *C. A.* **14**, 3145), all Fe being removed from some coals, but with others some silicate Fe was not extd. Decompn. of ankerites by heating to  $700^\circ$ ,  $800^\circ$ ,  $900^\circ$  gave approx. const. loss at  $800^\circ$  for 1.5 hrs. or at  $900^\circ$  for 1 hr. S. and S. conclude that the manner in which Fe occurs in coal varies widely. Five forms recognizable to date occur in ankerites as Fe oxide or carbonate, sol. Fe salts, silicates, and pyrites. Fe as pyrites predominates generally, but varies greatly. The amt. of silicate Fe was as high as 10% of the Fe in some coals, in others it was nil. The technic of the extn. and analytical methods used are given. A suggestive general discussion follows the article. W. H.

**The influence of a structure on the combustibility and other properties of solid fuels.** E. R. SUTCLIFFE AND EDGAR C. EVANS. *Colliery Guardian* **123**, 857(1922).—Tests made on ordinary raw coal, pitch-made briquets, and pure coal briquets made without binder showed a heat transmission per sq. ft. of grate area per hr. of 4070, 4039, and 4650 B.t.u., resp. The wt. of fuel burned per sq. ft. of grate per hr. was also much greater for the pure coal briquets. The chief factors in the combustibility of carbonized fuels are maintained to be: (1) influence of volatile matter, (2) influence of graphitic films on high-temp. coke, (3) influence of surface area, (4) porosity and (5) character of cell structure. The most desirable fuel is one as dense as possible with minute cells and a large no. of cells per unit mass. Gas coke is not ideal and its incombustibility is due primarily to the fact that the volatile products have to pass through the red-hot mass and deposit a film of graphite. C. C. DAVIS

**The constituent gases of smokes.** J. SEIGLE. *Rev. ind. minérale* No. 32, 207-14 (1922); cf. *C. A.* **15**, 2349; **16**, 1004. —The relation  $4.76 (\text{O}_2 + \text{CO}_2) + 2.88 \text{CO} - 0.88 \text{H}_2 + \text{H}_2\text{O} = 100$  cannot be applied to coals, hydrocarbons, etc., contg. O, H,  $\text{CO}_2$ , etc. For the latter cases there is derived the more complicated relation (the gases being expressed in % vol. as before):  $4.76 \text{O}_2 + (4.76 - K)\text{CO}_2 + (2.88 - K)\text{CO} - 0.88 \text{H}_2 + \text{H}_2\text{O} - (2.76 + K)\text{CH}_4 = 100$ , where  $K = [2(\text{O}_2 + \text{CO}_2) + \text{CO} - \text{H}_2] / [(2 \times 21)/79(1.86 + \text{CO}_2 + \text{CO})]$ . The gases in this last equation of  $K$  are in cu. m. per kg. of free C. The const.  $K$  becomes 0 when  $2(\text{O}_2 + \text{CO}_2) + \text{CO} - \text{H}_2 = 0$ , which is shown to occur in coke gas producers with a moist air blast. If the constituents accompanying the C in the combustible are expressed in wt., the value of  $K$  is shown to be:  $K = (0.7 \text{O}_2 + 0.51 \text{CO}_2 + 0.40 \text{CO} - 5.58 \text{H}_2) / (0.494 + 0.135 \text{CO}_2 + 2.12 \text{CO})$ . Applications to gasoline, EtOH, hard and soft coals, lignite and to gas producers are discussed. C. C. DAVIS

**Naphthalene as a motor fuel.** A. EBERT. *Schweiz. Chem. Ztg.* **1922**, 248-9.—Before it can be used in a motor, solid  $\text{C}_{10}\text{H}_8$  must be melted. Before stopping, the connections must be cleared. Hence such motors must start and stop on liquid fuel. Only dil. solns. in liquid fuels are practical for motor use.  $\text{C}_{10}\text{H}_8$  burns without residue, and equals liquid fuels in heating value. Hydrogenated  $\text{C}_{10}\text{H}_8$  is a valuable addn. to benzene, lowering its f. p. ERNEST W. THIELE

**Interim report of the Engineering Committee of the Empire Motor Fuels Committee.** W. R. ORMANDY. *J. Soc. Chem. Ind.* **41**, 223-3R (1922).—Tests for power, consumption and efficiency were made over a wide range of conditions, including varying compression, load, mixt. strength, piston speed, etc., using Ricardo's variable compression engine with alc. as the fuel. The results show clearly that in many directions alc. offers certain advantages over gasoline or benzene. At both high and low compressions the thermal efficiency of alc. is higher than with hydrocarbons and is almost independent of the speed. Tendency to preignition begins to be evident at 7:1 compression, and in practice 6.5:1 is probably the max. ratio which should be given to engines specially designed for this fuel. In all cases the running is much smoother than with hydrocarbon fuels. Alc. can be employed in all existing types of volatile-fuel engines from the paraffin engine upwards. In low compression engines the consumption of fuel is greater with alc. owing to its lower heat of combustion, but the consumption can be reduced greatly by increasing the compression. The cylinder is more easily kept cool when using alc., thus favoring power-output and efficiency. The presence of  $H_2O$  in alc. is also an advantage in this direction, and up to a piston-speed of 2000 per min. there is no evidence that the combustion is too slow to produce max. effect. Heat supplied to the carburetor at the rate of 3 h. p. somewhat reduced the power-output but slightly increased the thermal efficiency. No corrosive action was observed on any part of the engine as a result of using alc. under any conditions.

L. J. WILEY

**The blue flame produced by common salt on a coal fire.** W. HUGES. *Nature* **109**, 683 (1922).—Arguments are advanced to show that the blue flame which is seen when NaCl is thrown on a coal fire is due to CO produced by the cooling of the hot coal by the NaCl rather than to traces of Cu in the coal. ARTHUR SMITHELLS. *Ibid* 745.—The work of different investigators is quoted to show on the contrary that the blue color is due to  $CuCl_2$ , the source of the Cu being the pyrites of the coal. W. H. ROSS

**Extraction of Italian lignites by means of solvents.** PIETRO FALCIOLA. *Giorn. chim. ind. applicata* **3**, 546-8 (1921).—The percentage of exts. (compn. not given) obtained from lignite varied from 0.32 to 5.02, depending upon the conditions of the operation, the nature of the solvents, etc. The extns. were performed upon the finely divided dried materials in small amts. A bibliography is given on solvent extn. of natural combustibles.

ROBERT S. POSMONTIER

**Extraction of Italian lignites with solvents.** D. MENEGHINI. *Giorn. chim. ind. applicata* **4**, 203-4 (1922).—Powdered lignite, 20-30 g., previously dried at  $100^\circ$ , was extd. in a Soxhlet app. with  $C_6H_6$  (b.  $80.5^\circ$ ). The degree of fineness did not make much difference in extn. Extns. were made upon 20 different samples of lignite. A table shows the compn. of the lignites and gives  $H_2O$  of the samples dried in the air, ash, volatile substances,  $C_6H_6$  ext.; all except the first are based upon the wt. of the substances dried at  $100^\circ$ . The exts. freed of  $C_6H_6$  amounted to from 0.03 to 1.42%, one only going as high as 3.51%, and were of a brownish color tending to red, of waxy appearance, and of rather soft consistency; their  $C_6H_6$  solns. showed in almost all cases a greenish fluorescence. There was no relation between the % of volatile substance and amt. of ext. The results do not offer any hope that lignites may profitably be extd. with  $C_6H_6$ . M. does not indicate the compn. of the exts.

ROBERT S. POSMONTIER

**Indirect determination of the calorific value of naphtha used as fuel.** GIULIO MORRUCO. *Giorn. chim. ind. applicata* **4**, 15-7 (1921).—The analysis of a liquid combustible should include the following data: d<sub>15</sub>, viscosity at  $50^\circ$  and at  $100^\circ$ , point of inflammability, fractional distn. up to  $310^\circ$ , % fixed C, ash, S and  $H_2O$ . The calorific value may be obtained by use of the following formula: Cal =  $(11200a + 10300b + 8140c + 10000d + 2500e)/100$ , where  $a$  = fraction of hydrocarbons below  $110^\circ$ ,  $b$  = that between  $110^\circ$  and  $310^\circ$ ,  $d$  = that above  $310^\circ$  (by difference),  $c$  = % fixed C,  $e$  = % S.

ROBERT S. POSMONTIER

Distillation and rectification of a mixture of benzene, toluene and *m*-xylene. L. GAY. *Chimie et industrie* 7, 851-4(1922).—See C. A. 16, 1856. A. P.-C.

Carbonization report of 1921 Committee. J. H. TAUSSIG. *Tech. Sec. Am. Gas Assoc. 3rd Annual Convention* 3, 431-554(1921). Report of the Operators Section. W. H. EARLE. *Ibid* 432-41.—Operating data covering 19 plants of various types with recent developments in methods of oven and retort heating. Present status of coal-carbonization at low temperatures. J. D. DAVIS. *Ibid* 441-60; cf. C. A. 16, 331. Builders' section. F. G. CURFMAN. *Ibid* 461-548.—Descriptions are given by various authors of the Dessau vertical retort ovens, the Foundation Oven Corp's balanced draft coke ovens, the Gas Machinery carbonizing app., the Glover-West vertical retorts, the Improved Equipment Co. app., the Woodall-Duckham continuous vertical plant of the Isbell-Porter Co., the Koppers Ovens, the Piette ovens, the Russell Engineering Co. app., the Semet-Solvay ovens, and the U. G. I. Contracting Co. app. J. L. W.

Carbonization and gasification of peat. ANON. *Gas J.* 158, 566-7(1922).—From a report on the resources and industries of Ireland. Carbonization of peat has been carried out for the manuf. of illuminating gas and of peat charcoal. The former has not been successful on account of the high % of CO<sub>2</sub> in the gas and is no longer practiced. Charcoal making is, however, carried out extensively. 1000 lbs. of air-dry turf will produce 350 lbs. of charcoal, 40 of tar, 400 of tar liquors, and 210 of gas, with a thermal efficiency of 70%. The most efficient and economical method of developing power from peat is with the suction-producer and the gas-engine with recovery of the NH<sub>3</sub>. A consumption of about 3.5 lb. of peat will produce a b. h. p. hr. The next most efficient method, especially for large power stations, is that of direct-firing in a turbo-alternator unit. By constructing 4 power stations, each of 20000 kw. capacity, for the manuf. of CaCN<sub>2</sub>, Ireland's requirements of combined N would be more than satisfied. J. L. WILEY

Low-temperature carbonization. Work of the Fuel Research Board. GEO. BRILEY. *Gas World* 76, 439-40(1922); *Gas J.* 158, 500-1; *Iron Coal Trades Rev.* 104, 775-6.—The 2nd report 1920-21. Cf. C. A. 14, 2251. The report deals with the tech. and explt. developments in the low-temp. carbonization of coal. Consideration is given to the 3 principal products (oil, coke and gas) and the place of each in the economic and industrial success of the process. The use of the rich hydrocarbon gas for enrichment of lower grade gases establishes a link between the gas industry and low-temp. carbonization, and thus makes it one of the most valuable and least speculative assets of the latter industry. Furthermore, the study of the structure of the coke and of the influence on that structure of blending and prebriquetting has thrown new light on the origin and control of structure which may lead to practical and important developments and to the establishment of a link between low-temp. carbonization and the coking and metallurgical industries. Considerable emphasis has been given to these phases of the process and work is now being extended toward the development of automatic methods of carbonization, the study of briquetting as a preliminary to carbonization, and the development of a practical method of briquetting at or near the fusing point of the coal. Some work has also been done on detn. of the structure of coke. J. L. WILEY

Structure of coke: its origin and development. GEO. BRILEY. *Gas J.* 158, 558-60, 615-7; *Gas World* 76, No. 1976 (Coking Sec.), 15-6; *Iron & Coal Trades Rev.* 104, 811-12(1922); cf. preceding abstract.—B. describes the methods and app. used for studying the micro-structure and obtaining photomicrographs of coke by examg. thin transparent sections of coke under the microscope. Observations show that the sponge-like coke structure is due to the evolution of gas bubbles from the fused or partially fused coal substance, this development taking place continuously as the temp.

risers from 400° to 1000° or higher, depending upon the type of organic substance. For each type there is a stage in C concn. at which fusibility ceases and rigidity of the residue sets in. The study of the structure and properties of carbonaceous residues is much simplified by the knowledge that the C of which all forms of charcoal and coke are built up is a fairly homogeneous, vitreous solid, in which the vitreous properties become more rather than less marked as the state of elemental purity is approached, and further, that the bubble structure which is developed during the fluid or plastic stage of carbonization through the evolution of gases is finally stereotyped in this rigid vitreous material. Knowing the nature and origin of coke structure and the conditions which influence it, it can be so directed and controlled as to produce coke of any desired type. Formation of large bubbles only occurs when the froth is free to expand without the intervention of solid surfaces against which the bubbles burst, therefore in coke-oven practice, excessive foaming is arrested and a more homogeneous coke and one of finer and more uniform texture is obtained. This same result can be attained by blending coals of various fusibilities or by adding thereto pulverized coke or breeze. With the proper mixt. little or no foaming takes place and the resulting coke contracts in the oven. The proportions in which the selected coals should be mixed can be detd. by a few trials in the lab. assay app. (cf. Gray, C. A. 15, 1390). J. L. WILEY

**Low-temperature carbonization of South African coal.** ANON. *Iron & Coal Trades Rev.* 104, 853(1922).—Of 9 samples of Natal and Transvaal coals investigated at the Greenwich Fuel Research Station, 8 were found to be suitable for carbonization at low temps. (600°), yielding a fairly strong coke. The coals were all similar in appearance, being of a mixed character and composed of alternate layers of bright, soft and dull hard coal. The yield of coke varied from 14.8 to 16.6 cwt. per ton. The yields of gas, with a high content of unsatd. hydrocarbons, were rather low but of good quality (about 1000 B.t.u. per ft.<sup>3</sup>). The tars were typical low-temp. tars and the yields were 10.3 to 15.7 gal. per ton. (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> yields were low, 3.2 to 5.8 lbs. per ton in the type of horizontal retorts used at the station. J. L. WILEY

**Some remarks on low-temperature carbonizing.** HARALD NIELSEN. *Gas J.* 158, 446-7(1922).—See C. A. 16, 2200. J. L. WILEY

**A symposium on low-temperature carbonization of coal.** The national importance of low-temperature carbonization. DAVID BROWNLEE. Low-temperature carbonization of coal, etc. WM. E. DAVIES. Low-temperature carbonization of coal. N. H. FREEMAN. The "fusion" patent low-temperature retort. C. J. GOODWIN. Low-temperature carbonization of coal. S. R. ILLINGWORTH. The Maclaurin carbonizing process. ANON. Low-temperature carbonizing. HARALD NIELSEN. Improved low-temperature by-product recovery gas product process. ANON. Economic aspects of low-temperature carbonization. JOHN ROBERTS. Low- versus high-temperature carbonization for the production of smokeless fuel. E. R. SUTCLIFFE AND E. C. EVANS. *Colliery Guardian* 123, 979-81, 1041-3(1922).—General discussions of present practice. C. C. DAVIS

**Studies in the carbonization of coal: Characteristics of low-temperature tar.** J. J. MORGAN AND R. P. SOULE. *Chem. Met. Eng.* 26, 923-8, 977-81(1922).—This paper deals with an intensive investigation of a commercial low-temp. coal tar (carbolic process) and gives a scheme by which the component groups may be readily examd. By this scheme the compn. of the distillate up to 326° is phenols 42.7%, bases 1.94%, cyclic unsatd. hydrocarbons 41.5%, naphthenes 8.8%, paraffins 5.1%. On basis of crude dry tar these percentages are: 13.7, 0.624, 13.4, 2.8 and 1.6. The distn. curve for the tar is similar to the curves of gas-retort and coke-oven tars, disproving claims of high yields of low-boiling oils in low-temp. tar. Analysis of the phenols gave, on the basis of the crude dry tar, phenol 0.6%, cresols 4.9% (27% o-, 19% m-, and 54% p-), xylene



fraction 2.8%, higher homologs 5.1%. The higher homologs are naphthol derivs. but contain no naphthol. Comparison with other analyses shows that the amt. of phenols in low-temp. tars increases with the yield of tar from the coal carbonized, the quantity of non-phenolic oils remaining relatively const. In general coals of highest volatile matter yield the most phenols. The bases are 80% tertiary and 20% secondary, both unsatd. with no primary bases. No preponderant base is present. Pyridine was detected, but the higher boiling bases differ from those of ordinary coal tar by having lower ds. and higher mol. wts. These differences are ascribed to the presence in the low-temp. bases of partly hydrogenated nuclei and of side-chains longer than those in high-temp. bases. No alcs. are present.  $\text{H}_2\text{S}$  is present but  $\text{CS}_2$  is not. Thiophene is indeterminate in the presence of unsatd. hydrocarbons. The neutral oils of low-temp. tar are characterized by low d. and viscosity and by absence of more than traces of compds. solid above  $-30^\circ$ . No single hydrocarbon preponderates. Unsatd. hydrocarbons are present and on standing cause darkening and increased d. of the oil. The satd. and unsatd. hydrocarbons were sepd. by 98%  $\text{H}_2\text{SO}_4$ , correction being made for polymerization. The proportion of naphthenes was detd. from the sp. gr. of the residual satd. hydrocarbons. The non-satd. hydrocarbons, recovered by liquid  $\text{SO}_2$ , were shown by d.,  $\pi$  and mol. wt. to belong to the same series as that found by Pictet in vacuum tar. Solid aromatic hydrocarbons are absent. Liquid aromatics can be present only in traces. Many tables and curves are given.

JEROME J. MORGAN

**Studies in the carbonization of coal: The mechanism of coal carbonization.** J. J. MORGAN AND R. P. SOULE. *Chem. Met. Eng.* 26, 1025-30(1922).—Review of the theories of the constitution of coal and of carbonization reactions is given. The bearing of the results of an examn. of a com. low-temp. tar (preceding abstract) on these theories is considered. It is suggested that the chem. properties of coal may be represented by a structure contg. many six-membered cycles. This structure may be pictured as an aggregate of "mosaics" of these rings joined by bridges of paraffin hydrocarbons and O-, N- or S-contg. groups. In the carbonization of coal the remnants of the breaking of these bridges account for the numerous side-chains which are characteristic of low-temp. tar. Further: (1) The decompn. of coal by heat to ordinary high-temp. tar is a progressive, step-by-step decompn., in which pyrogenetic syntheses play only a secondary part. (2) Six-membered rings and their combinations characterize the entire series of decompn. products from coal to high-temp. tar. The decompns. are essentially reactions effecting elimination of side-chains. (3) The av. mol. wt. of the liquid products constantly decreases as the temp. of carbonization rises. This decrease is marked by evolution of  $\text{H}$ ,  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$ . (4) The initial decompn. of the primary low-temp. tar is (a) loss of  $\text{H}$  from naphthenes with a resultant increase in unsatd. hydrocarbons; (b) loss of side-chains from phenols by hydrogenation with formation of lower-boiling phenols; (c) loss of  $\text{H}$  from nitrogen bases with formation of tertiary bases. This stage is represented by carbocoal tar. (5) Final decompns. are at a maximum between  $700^\circ$  and  $800^\circ$ , and are marked by (a) dehydrogenation and dealylation of the hydroaromatic unsatd. hydrocarbons and bases to form aromatics, with the elimination of  $\text{H}$ ,  $\text{CH}_4$  and other simple gases; (b) hydrogenation of phenols to aromatic hydrocarbons and of these to lower boiling aromatics, with formation of  $\text{H}_2\text{O}$ ,  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$ ; (c) secondary pyrogenetic syntheses of higher aromatics from simple compds. (6) The phenols of low-temp. tar are the principal source of monocyclic aromatic hydrocarbons. The unsatd. naphthenes of low-temp. tar are the principal source of polycyclic aromatics.

J. J. MORGAN

**Low-temperature carbonization of coal.** W. EVERARD DAVIES. *Gas J.* 158, 447-8(1922).—See C. A. 16, 1308.

J. L. WILEY

**Utilization of compressed air in clearing gas piping.** J. T. GRIFFIN. *Tech. Sec.*

*Am. Gas Assoc. 3rd Annual Convention 3*, 143-60(1921).—Compressed air at a pressure of 1500 lbs. is used for removing stoppages in service pipes, and scale from house heating boilers, and for blowing out obstructed drain pipes to sewers. J. L. WILEY

**Increasing distribution capacities.** C. N. CHUBB. *Tech. Sec. Am. Gas Assoc. 3rd Annual Convention 3*, 103-42(1921).—A discussion is given of gas pressure boosting, compressing and pumping equipment; comparison between district holder vs. district governor distribution, with recent developments on automatic loading of district governors; max. pressure desirable on low pressure mains, and at the burner. J. L. W.

**Disposal of waste from gas plants.** F. W. SPERR, JR. *Tech. Sec. Am. Gas Assoc. 3rd Annual Convention 3*, 571-95(1921); cf. *C. A.* 16, 155. J. L. WILEY

**Deposits in the gas pipes and meters.** O. A. MORHOUS. *Tech. Sec. Am. Gas Assoc. 3rd Annual Convention 3*, 555-70(1921).—A general progress report. J. L. WILEY

**The preparation of gases of high heating value by treatment of distillation gases with active carbon.** FRANZ FISCHER, HANS SCHRADER AND CARL ZERBE. *Brennstoff Chem.* 3, 145-7(1922).—Gas from the low-temp. distn. of coal was passed at the rate of 6 l. per min. through 678 g. of Bayer's active C, at an av. pressure of 16 atms. When 350 l. (measured at atm. pressure) had passed through, the gas adsorbed on the C was removed, first by relieving the pressure and then by gradually heating to 300°. The heating value of the various fractions was as follows: original gas, 7320 Cal. per cu. m., first 20 l. relieved, 7880; further 10 l. relieved, 9050; heated to 50°, 9600; to 75°, 11200; to 100°, 13100 (vol. driven off up to 100°, 19.5 l.); to 125°, 9.5 l., 19900; to 300°, 1.4 l., 18100; total vol. recovered with increased heating value, 63.5 l. An illuminating gas from Mülheim coke ovens was similarly treated at about 18 atm. av. pressure; out of a total quantity of 432.5 l., of heating value 4770, 19.7 l. was recovered on relieving pressure, heating value 5190; heating to 100°, 9.2 l., 10900; to 200°, 3.2 l., 15420; to 300°, 0.4 l., 17500; total vol. recovered, 32.5 l. W. B. V.

**Bergmann's gas-producing stoker.** NETTMANN. *Z. Ver. deut. Ing.* 66, 131-2 (1922).—The construction is such that the fuel in the sloping firebox passes through the temporary succession of steps of drying, smoldering, gasifying and burning. Air for combustion is preheated before coming into the fuel zone consisting of the semi-coke and gas that has been previously produced. Several installations have been made and tested over a 6 months period. With a flue gas temp. of 200° an efficiency of 75% has been obtained and 80 to 82% is assured. The flue gas contained 13 to 15% CO<sub>2</sub>. A grate surface of 1 sq. ft. ordinarily will handle 140 to 210 lbs. per hour, while a sq. ft. of the sloping grate will care for 45 to 70 lbs. of a mixt. of brown coal and hard coal per hr.; 70 lbs. of brown coal briquets per hr.; 140 lbs. of peat per hr.; and from 120 to 380 lbs. of crude brown coal per hr. ARTHUR L. DAVIS

**Tests of gas-saving devices.** ANON. *Am. Gas J.* 116, 530-1, 534(1922).—As a result of tests made by the Bur. Standards on some of the so-called gas-saving devices for domestic gas burners, it is shown that no marked increase of efficiency can be expected from their use. In cases where the burners are far below the grid or where the pressure drops far below that for which the burner is adjusted some increase in efficiency will result, but this is in no case very large and can in no way justify the claims of economy made by the makers. Furthermore, these devices break up the flames as they leave the ports, mix the flames into one mass and by so doing exclude to a large extent the supply of secondary air necessary for complete combustion. The poor aeration of the flame results in rapid liberation of CO in sufficient quantity to be a positive menace to health. J. L. WILEY

**The Foxwell theory of the path of travel of the gases in the coke oven.** G. E. FOXWELL. *Gas World* 76, No. 1976 (Coking Sec.), 10(1922).—A less mathematical sketch of the theory than described in *C. A.* 16, 156. Cf. Biddulph-Smith, *C. A.* 16, 2208. J. L. WILEY

**Portable demonstrating water-gas set.** EDWARD H. BAUER. *Am. Gas Assoc. Monthly* 4, 251-4(1922).—A detailed description with diagram is given of the construction and operation of a complete carbureted water-gas set from blower to cooled gas, including a steam boiler which furnishes steam to the generator and oil pump, and reservoir from which oil is pumped into the combined carburetor and superheater.

J. L. WILEY

**Producer gas for by-product ovens.** FREEMAN D. LOHR. *Gas Age-Record* 49, 677-81(1922).—The Koppers-Kerperly gas producer plant of the Seaboard By-Product Coke Co. is described and operating data are given. The gas is cooled and cleaned before being used to heat the coke ovens, and gives an entirely satisfactory heating service with a min. fuel and C consumption per ton of coal carbonized. The plant is entirely self-sustaining as regards steam requirements.

J. L. WILEY

**Collecting gas samples.** SCHUMACHER. *Gas u. Wasserfach*. 65, 218; *Gas J.* 158, 203(1922); 2 figs.—Two app. are described for taking gas samples. The first enables an av. sample to be taken over a period of gas production lasting several hrs. The gas flow is kept at a const. rate by regulating the flow of water from the collecting tank by a special device and at the desired speed. The 2nd app. is for use in taking gas samples from wells or shafts.

J. L. WILEY

**Report on liquid purification.** A. M. BEEBE, et al. *Gas Age-Record* 49, 741-3(1922).—B. reviews the operation of each of the Seaboard processes (*C. A.* 16, 482) and the O'Neill process (*C. A.* 6, 3007; 7, 410; 8, 2474). Neither system has yet been found to be very efficient as total S removers but they do remove substances which lower the activity of the oxide of the oxide boxes and are very efficient in CN removal.

J. L. WILEY

**Gas purification. Report of 1921 Committee.** A. C. FIELDNER. *Tech. Sec. Am. Gas Assoc. 3rd Annual Convention* 3, 189-281(1921).—Summary of results accomplished. **Activity and capacity of oxides.** W. A. DUNKLEY. *Ibid* 198-208.—A modification of the Kunberger test is proposed in which 1 g. of oxide is subjected to an excess of pure  $H_2S$  for 1 min. only, the activity being expressed by the % of  $H_2S$  absorbed per unit wt. of  $Fe_2O_3$ . The agreement in the results of this method of several investigators is very close. **Determination of activity of oxides by rate of flow.** A. R. POWELL. *Ibid* 209-13.—A second method is to det. the max. flow of a dil. mixt. of  $H_2S$  in an inert gas, at which a standard quantity of the unfouled oxide removes the  $H_2S$  completely. With the same oxides as used in the above test, the results did not differ greatly. **Effect of moisture on the activity and capacity of iron oxides for gas purification.** W. A. DUNKLEY. *Ibid* 214-41; cf. *C. A.* 16, 154. **Bibliography on gas purification.** A. R. POWELL AND K. C. WALKER. *Ibid* 242-67.

J. L. WILEY

**By-product gas industrial uses.** HARRY DOBRIN. *Gas Age-Record* 49, 719-22(1922); cf. *C. A.* 16, 1496.

J. L. WILEY

**Seaboard liquid process of gas purification.** F. W. SPERR, JR. *Tech. Sec. Am. Gas Assoc. 3rd Annual Convention* 3, 282-385(1921); cf. *C. A.* 16, 482. **Résumé of literature on liquid purification.** D. L. JACOBSON. *Ibid* 353-63.

J. L. WILEY

**Report of the Technical Committee on Gas Oil.** W. H. FULWEILER. *Tech. Sec. Am. Gas Assoc. 3rd Annual Convention* 3, 82-93(1921).—Data on production, tests and analyses are given.

J. L. WILEY

**Refractory materials.** W. H. FULWEILER. *Tech. Sec. Am. Gas Assoc. 3rd Annual Convention* 3, 94-100(1921).—See *C. A.* 16, 636.

J. L. WILEY

**What goes on in a water-gas machine?** M. E. BENESH. *Tech. Sec. Am. Gas Assoc. 3rd Annual Convention* 3, 9-38(1921).—See *C. A.* 15, 3901.

J. L. WILEY

**Ash-fusion gas-producer.** A. FICHT. *J. usines gas* 46, 1-7(1922); *Am. Gas J.* 116, 550-2.—The development of this type of producer is traced and its operation

described. The thermal efficiency of the process is 95.5%. It is possible to construct such producers capable of gasifying 2500 kg. of fuel per hr. Coal of very poor quality can be used. Owing to the advantages in construction, ease of operation, good quality of gas produced, efficiency of gasification, and low initial cost, the ash-fusion producer is the logical type of gas producer of the future.

J. L. WILEY

**Benzene purification.** S. S. HEDGE. *J. Ind. Eng. Chem.* **14**, 491-2(1922).—A general explanation of the process. Benzene which is c. p. can be made direct from the crude motor benzene fraction, contg. all the benzene, toluene, and light solvent present in the original light oil, by washing and distg. The products give better color tests than are obtained by washing and distg. the 90% crude benzene fraction, less acid is required, a better sepn. is obtained in the agitator, and very good yields of c. p. benzene are obtained.

J. L. WILEY

**Factors affecting the efficiency of gas producers working on bituminous coal.** ANON. *Iron Coal Trades Rev.* **104**, 856-7(1922).—Assuming that the fuel gasified is of reasonably satisfactory character (non-coking or low-coking coal with a low % of relatively infusible ash), and that the fuel bed is maintained in proper condition, the working of the producer, and the quality of gas generated are mainly detd. by the rate of gasification and the blast satn. temp. and are independent of the means used for blast satn. The blast satn. temp. is of the greatest importance in controlling and detg. the working of gas producers, and thermometers should in all cases be fitted to each producer to indicate the proportion of steam used. The tests show that with Shropshire and South Yorkshire coals, blast satd. at a temp. of about 55° gives gas of high calorific value and of suitable compn. for furnace work. At this temp. and with reasonable rates of gasification, there is likely to be little trouble from the formation of clinker. When live steam must be used for satg. the blast, and when the blast furnace pressure does not exceed 2 in. water gage, a simple type of solid jet may give the required blast satn. temp. Jets of this type are easily regulated and appear to give a nearly const. temp. when the vol. delivered is varied within fairly wide limits. They are not, however, suitable for injection against high back-pressure and, if badly designed or fitted, or if used under unsuitable conditions, may give satn. temps. considerably in excess of 55° with resultant waste of steam and reduced efficiency of the plant. When working against increased blast pressures, blowers of the annular or multi-jet type are more efficient. If the blast satn. temp. then becomes too low, when used with low blast pressures, the proportion of steam can be increased by restricting the air supply to the blast furnace pipe or by providing a secondary addition of steam. In all cases indication of the blast satn. temp. is essential to correct adjustment. Positive blast from a mech. blower can be used against increased pressures and, with suitable regulation, the satn. temp. can be satisfactorily controlled. The whole of the steam used may be exhaust steam. The trials indicate the necessity for maintaining a const. pressure on the steam main when steam-jet blowers are used. The variations in boiler pressure may cause a marked fluctuation in the amt. of gas generated, thus resulting in waste. A reducing valve should always be provided to maintain a const. pressure in the steam supply main at the producers.

J. L. WILEY

**Developments in the use of paraffin for coast lighting.** ANON. *Engineering* **113**, 541-4(1922), illus.—Where lights of high power are required, electricity and paraffin oil are the usual illuminating agents used; the latter is by far the most economically efficient method. The general uses of lighthouse optical app. are described and the development of the oil burner up to the present time is traced. The Hood incandescent autoform mantle burner with vaporization in a pre-heated vaporizer is described in detail. The mantle is made from viscose silk impregnated with Th and Ce and is specially treated to withstand the pressure from the Bunsen flame. Until it is placed

on the burner it is quite pliable and can be packed for transport without any special care. It is made in 4 sizes: 35, 50, 75 and 100 mm., with projected areas of 11, 7, 3.5 and 2 sq. in., resp., and when illuminated possesses an intrinsic brightness of 300 to 330 candles per sq. in., or an increase of 100% over that of the collodion mantle and 1300% over Fresnel's 4-wick burner. The cost of repairs is only about one-tenth that of other types. The British specification for paraffin oil for lighting is a flash point of 150° F. and a sp. gr. of 0.805.

J. L. WILBY

**Dempster-Toogood vertical retorts at Batley.** ANON. *Gas World* **76**, 425-6 (1922); *Gas J.* **158**, 441-3.

J. L. WILBY

**Neutralization of sulfate of ammonia.** THOMAS JOHNSON. *Colliery Guardian* **123**, 598-9 (1922).—A description of the  $(\text{NH}_4)_2\text{SO}_4$  plant at Langley Park, England. This is of the direct type and even in summer the saturator can be worked without the use of a superheater for keeping down mother liquor. Cf. *C. A.* **16**, 1655. C. C. DAVIS

**Kuroda's by-product regenerative coke oven.** TAIZO KURODA AND HIROSHI OHNO. *J. Chem. Ind. (Japan)* **24**, 875-83 (1921).—The oven constructed in a Japanese steel plant is described. The devices to heat the coal uniformly at a high temp., and to conduct the dry distn. in as short a time as possible are the main features. Several technical features of their operation are given in detail. The air for combustion enters the regenerators from the passage at the front and the back of the ovens. From the regenerators it passes into the horizontal flues, whence it is distributed into the vertical heating flues. The gas from the by-product plant is returned to the ovens by the gas main, which runs along the whole length of the ovens on either side. When the reversing cocks are in such a position that the gas can be supplied to one of the distributing gas flues, which consists of two independent canals, the gas passes through the gas nozzles into the vertical heating flues, which are divided into 15 independent parts with two sections. The mixt. of gas and air burns in one section of each vertical part, and the products of combustion make their way down the other section, are collected in the horizontal flues from each opening, by which the air is admitted to flues when the direction of combustions is reversed, and enter the regenerators. At the end of about half an hour, the reversing cocks, the air valves and the dampers are simultaneously reversed by means of the winch. In the latest design the horizontal flues are omitted. The cost of manuf. of coke is  $\frac{1}{2}$  of that of Kopper's type. S. T.

**Refractories for coke-oven practice.** W. J. REES. *Chem. Trade J.* **70**, 326-7 (1922).—Assuming proper selection of the brick, the advantages of silica brick for oven construction may be summed up as follows: (1) Resistance to corrosion where salty coals are coked, (2) the possibility of increased output due to higher thermal efficiency, (3) the greater durability more particularly under high-temp. coking conditions. The silica brick analyzed about 94-97%  $\text{SiO}_2$  and 1.8-2.5%  $\text{CaO}$ . E. F. P.

**Recovery and utilization of cyanide from by-product coke ovens.** EDWARD V. ESPENHAHN. *Chem. Met. Eng.* **26**, 938-41 (1922).—Discussion of the consumption and uses of cyanides and description of the E. process for recovery of cyanides from coal gas as HCN or NaCN. Coke-oven gas contains 70-75 grains HCN per 100 cu. ft., yielding 1 lb. HCN or 1.75 lb. NaCN per ton of coal. The gas, preferably after it is freed from  $\text{NH}_3$ , is scrubbed in centrifugal washers with a strong soln. of  $\text{Na}_2\text{CO}_3$  in which is suspended  $\text{FeS}$  or  $\text{Na}_2\text{Fe}(\text{CN})_6$ . The resulting soln. of  $\text{Na}_2\text{CO}_3$  and  $\text{Na}_4\text{Fe}(\text{CN})_6$  is filtered and cooled.  $\text{Na}_4\text{Fe}(\text{CN})_6$  alone crystallizes, is centrifuged and treated with  $\text{H}_2\text{SO}_4$ .  $2\text{Na}_4\text{Fe}(\text{CN})_6 + 3\text{H}_2\text{SO}_4 = \text{Na}_2\text{FeFe}(\text{CN})_6 + 3\text{Na}_2\text{SO}_4 + 6\text{HCN}$ . The HCN is liquefied or absorbed as NaCN in a soln. of  $\text{Na}_2\text{CO}_3$  or  $\text{Na}_2\text{SO}_4$  contg. an equiv. of  $\text{Ca}(\text{OH})_2$ . The pptd.  $\text{Na}_2\text{FeFe}(\text{CN})_6$  is washed free from  $\text{Na}_2\text{SO}_4$  and returned to the washers. The process, which has not yet reached a semicommercial scale, might be economically applied to large coke-oven plants, and could thus produce the equiv.

of 20,000 tons of NaCN per year, which is more than present consumption. Estd. costs are much lower than those for synthetic cyanides. JEROME J. MORGAN

**Thermal dissociation of ammonia with special reference to coke oven conditions.** G. E. FOXWELL. *J. Soc. Chem. Ind.* **41**, 114-25T(1922).—Very little previous work has been done on the subject from the standpoint of velocity of reaction. The exptl. method consisted of passing coal gas with definite concns. of  $\text{NH}_3$  through a heated quartz tube contg. coke or fire brick. The results show: (1) The reaction when excess of solid surface is present is bimolecular. (2) When  $\text{NH}_3$  dild. with coal gas is passed over coke, the velocity of decompn. increases slowly with the temp.; the coeff. is 1.136. The value of the velocity const.,  $k$ , can be expressed by the Arrhenius formula,  $k_1 = k_2 e^{A(\frac{1}{T_1} - \frac{1}{T_2})}$ , where  $A = 13,300$ . (3) For narrow tubes ( $<0.5$  cm. radius)  $k \propto 1/r$ , but it seems probable that for wide tubes  $k \propto 1/r$ . (4) When gases contg.  $\text{NH}_3$  are passed through porous material the amt. of decompn. in unit time varies directly as the square of the radius of the pores; hence it is the size of the pores rather than the total porosity that is of importance. (5) Silica brick have less decomposing effect than siliceous brick. Iron in brick is very harmful. (6) The compn. of the ash of the coal affects the rate of decompn. Rutile and feldspar have little, if any, action.  $\text{FeS}_2$  is converted into FeS during carbonization and this somewhat increases the velocity. Iron oxide, which is converted to Fe, greatly increases the rate of decompn. as does lime to a less extent. The action of NaCl is complicated. (7) For the purpose of further investigation the value of  $k$  for coke will be taken as 0.00200 at  $755^\circ$ . From a discussion of these results and those of a previous paper (*C. A.* **16**, 156) the following conclusions are drawn: The effect of water added with the coal is to cause more gas to travel up the hot zone, and although the final concn. of  $\text{NH}_3$  in the gas of the hot zone is greater with wet coal, the total amt. of  $\text{NH}_3$  decompd. is also greater. If the reaction were monomolecular very little  $\text{NH}_3$  would be recovered. Increasing the height or width of the oven has little effect on the yield of  $\text{NH}_3$ . In regard to temp. of carbonization, low yields of  $\text{NH}_3$  result from too low temp. because the  $\text{NH}_3$  is not formed, from too high temp. because it is decompd. Salt in coal yields HCl which is a negative catalyst in the decompn. of  $\text{NH}_3$ . In the free space of the coke oven the velocity of decompn. of  $\text{NH}_3$  is small, but because of an eddying motion forcing the gas against the walls it is important to use brick low in Fe for the roof and upper parts of walls.

J. J. MORGAN

KALLENBERG, OTTO: **Der praktische Gas- und Wasserinstallateur.** 2nd Ed. Stuttgart: Ernst Heinrich Moritz (Jnh. Franz Mittelbach). Paper cover M 15, bound M 60. 368 pp. Reviewed in *Gas. u. Wasserfach.* **65**, 95(1922).

BEST, WM. NEWTON: **Burning Liquid Fuel.** New York: "Metal Industry" 99 John St. 341 pp. \$5. Reviewed in *Metal Ind.* **20**, 191(1922).

SCHILLING, E. and THIEM, G.: **Kalender für das Gas- und Wasserfach.** 2 parts. München: Oldenbourg. In pocket form M 50. Reviewed in *Gesundh. Ing.* **45**, 192(1922).

HOBHN, ERNST: **Chauffage aux combustibles liquides.** Paris—Liège: Ch. Béranger 29 pp. Fr. 2.

**Apparatus for heating by combustion without flame.** M. MATHY. Can. 218,819, May 23, 1922. Means are provided for the flameless combustion of a gaseous mixt. in a mass of fragments of porous material such that the size of the fragments at each part to be heated is less as the temp. desired is higher.

**Regenerative furnace retort.** C. H. SMITH and E. B. EDWARDS. U. S. 1,417,113, May 23.

## 22—PETROLEUM, ASPHALT AND WOOD PRODUCTS

F. M. ROGERS

**Corrosion of petroleum refining equipment.** R. R. MATTHEWS AND P. A. CROSBY. *Chem. Met. Eng.* 26, 1119-20(1922); cf. *C. A.* 15, 749.—Hydrolysis of  $MgCl_2$  with formation of HCl is probably the main cause of the corrosion of petroleum refinery condensers and heat-exchangers. After  $2\frac{1}{2}$  years of intermittent service the upper part of the steel tubes of the condensers serving stills No.'s 4 and 5 of an eight-still continuous battery were found to be so badly corroded on the oil-vapor side that they leaked. The temp. of the oil in these stills ranged from  $177^\circ$  to  $260^\circ$ . Lab. tests showed that a mixt. of anhydrous oil and hydrated  $MgCl_2$  crystals started to evolve HCl at  $175^\circ$ . The use of steam increases hydrolysis and promotes corrosion. Tubes in a heat-exchanger operating at about  $110^\circ$  were also badly corroded on the crude-oil side. The best preventive of condenser-tube corrosion so far devised is the introduction of  $NH_4$ . A better remedy would be the complete removal of the salt-water from the crude petroleum.

E. H. LESLIE

**Shale industries in Germany, France, Great Britain and Norway.** SVEN V. BERGH AND K. E. LARSON. *Teknisk Tidskrift* 52, 305-15(1922).—Report of a tour of inspection. Maps, photographs, sketches and several analyses.

A. R. ROSE

**The isolation of organic substances in Estonian oil shales.** J. NARBUTT. *Z. angew. Chem.* 35, 238-9(1922).—Powd. shale was evapd. to dryness with HCl, extd. in a Soxhlet app. with MeOH until no reaction with  $(NH_4)_2S$  occurred. The residue was then dried, evapd. with HF and later repeatedly with HCl. The mixt. of org. matter and salts was washed with hot water contg. HCl, and again extd. with MeOH in a Soxhlet app. The org. matter (about  $\frac{1}{2}$  the original material) was obtained quantitatively. It is a dark brown powder, d. less than 1, yields 2.5% of ash (chiefly  $Fe_2O_3$ ), is partly sol. in aromatic hydrocarbons like naphthalene and phenanthrene at  $300-330^\circ$ , with partial decomp., and, when heated alone to  $300-350^\circ$ , decomposes into a clear brown oil and a carbonaceous residue, and evolves a gas contg.  $H_2S$ .

W. C. EBAUGH

**Forest products industries of the South.** CARLILE P. WINSLOW. *Chem. Age* (N. Y.) 30, 145-9(1922).—W. gives warning of the depletion of the Southern pine forests and suggests remedial measures. The role of chemistry in conservation of timber resources is outlined, special reference being made to chemical utilization of wood waste and of timber preservation.

L. E. WISE

**Wood turpentine.** C. A. LAMBERT. *J. Ind. Eng. Chem.* 14, 491(1922).—An abstract. The physical properties and chem. compn. of crude and purified wood turpentine, as well as the physical properties of "pine-oil," are given.

L. E. WISE

**The oxidation of wood and the aging of wood for violins.** S. ARNDT. *Z. Sauerstoff-Ind.* 13, 53-4 (July 1921); *Chimie et industrie* 7, 941(1922).—Expts. on the oxidation (by  $O_2$ , etc.) of wood for string instruments to improve the tone and expression have shown that there is no destruction of the resin. Oxidation, whether slow or rapid, seems to render the resin fluid, so that it is easily distributed throughout the vessels of the wood, and the compn. of the latter becomes more homogeneous. Natural oxidation of the resin is not complete after 50 yrs. Oxidation manifestly improves the acoustic properties of wood. A. has devised a method of improving the expression of string instruments by aging the wood before using it. The nature of the oxidizing agents used is kept secret.

A. P.-C.

**Application of electrical precipitation to the wood-distillation process.** L. F. HAWLEY AND H. M. PIER. *Chem. Met. Eng.* 26, 1031-3(1922).—Preliminary small-scale expts. are described which indicate the possibility of pptg. a large part of the tar from

the hot vapors obtained in wood distn. by means of a Cottrell precipitator. The pyro-ligneous acid thus obtained contained much less soluble tar (3.3% instead of 12–15%), but did not yield a satisfactory Ca acetate on direct neutralization. The defects of the exptl. equipment and the possibility of eliminating these defects in commercial scale app. are discussed.

I. R. WISE

**Refining petroleum.** P. T. SHARPLES. U. S. 1,416,890, May 23. A petroleum residue obtained by distg. off gas, naphtha and burning oils from crude petroleum without substantially cracking the residue is chilled to ppt. the wax which it contains and the chilled residue is subjected to centrifugal sepn. to free the liquid components from the wax. U. S., 1,416,891 also relates to centrifugal sepn. of pptd. wax from a non-cracked petroleum residuum.

## 23—CELLULOSE AND PAPER

CLARENCE J. WEST

**Industrial preparation of cellulose by the chlorine method.** A. CERRUTI. *Giorn. chim. ind. applicata* 4, 64–5(1922).—Short critical review. ROBERT S. POSMONTIER

**Industry of chlorine-process cellulose.** UMBERTO POMILIO. *Giorn. chim. ind. applicata* 4, 207–10(1922).—Argumentative on the industrial and economic bearings of the process. ROBERT S. POSMONTIER

**Industrial balance of chlorine-process cellulose.** ALESSANDRO CERRUTI. *Giorn. chim. ind. applicata* 4, 211–2(1922).—Reply to article of Pomilio (preceding abstract). ROBERT S. POSMONTIER

**Transformation of the cellulose complex in the manufacture of artificial silk.** WALTER VIEWEG. *Zellstoff u. Papier* 2, 18–9(1922).—When cellulose is introduced into 18% NaOH there is formed the complex  $(C_6H_7O_5)_2 \cdot NaOH$  which, upon pressing out, is changed to  $(C_6H_7O_5)_2 \cdot NaOH$ . The addn. of  $CS_2$  gives the complex  $(C_6H_7O_5)_3 \cdot CS_2 \cdot NaOH$ . In the soln. which can be spinned, the cellulose is probably present as  $(C_6H_7O_5)_4$ . C. J. WEST

**The solubility of cellulose acetate in salts of the alkali and alkaline earth metals.** K. SCHWIEGER. *Z. physiol. Chem.* 117, 61–66(1921).—The solubilities of a number of com. preps. were detd. in LiBr, LiI, NaI, BaBr<sub>2</sub>, CaI<sub>2</sub>, Ca(NO<sub>3</sub>)<sub>2</sub>, Ca(CNS)<sub>2</sub>, KHgI<sub>4</sub>, and ZnCl<sub>2</sub> at 15° and 100°. They differed for the various preps. in the same solvent. In Ca(CNS)<sub>2</sub> 20–30% solns. could be obtained. Solns. prepd. at higher temps. were more viscous than those prepd. at lower. There is no action of the salt solns. on the Ac groups but some splitting of the cellulose mol. itself occurs. R. L. STEINLE

**The determination of α-cellulose.** WAENTIG. *Zellstoff u. Papier* 2, 12–7(1922).—The factors influencing the detn. of α-cellulose are proportion of cellulose to liquor, the degree of fineness of the cellulose, the time and the temperature of the liquor and the method of washing the residue. Three g. of cellulose to 30 g. liquor at 18° are recommended. At the close of the mercerization the whole should be poured into 5 volumes of water and washed according to Jentgen (*Kunststoffe* 1911, 165; cf. C. A. 7, 3049).

C. J. WEST

**Determination of the cellulose content of wood and other raw materials by the action of chlorine in carbon tetrachloride.** E. HEUSER AND H. CASSEUS. *Papier-fabr., Fest- u. Auslandheft* 1922, 80–93; cf. C. A. 16, 340.—This method is based on German patent 323,936 (A. Frank). At the ordinary temp. a satd. soln. of Cl in CCl<sub>4</sub> contains 8.1 g. Cl per 100 cc. CCl<sub>4</sub>; after standing 4 wks. in a closed flask, the Cl content



was 7.80 g. Cl. It is shown that it is unnecessary to make a preliminary ext. with  $\text{CaH}_2\text{-EtOH}$ , since the fats and resins are removed by the  $\text{CCl}_4$ . 1.2-1.5 g. of medium fine material (this filters better than fine) are shaken with 50 cc. satd.  $\text{Cl-CCl}_4$  for 1-2 hrs.; the fiber is filtered and washed with  $\text{CCl}_4$ ,  $\text{EtOH}$  and then  $\text{H}_2\text{O}$ . The lignin chloride is then dissolved out with 2%  $\text{Na}_2\text{SO}_3$ , the product washed with  $\text{H}_2\text{O}$ , dried and weighed. The Cu no. of the product varied between 0.8 and 0.91 as compared with 3.14 to 3.23 by the older method. It is lignin-free, and contains 3 to 3.5% pentosan. The actual yield of pure cellulose was, therefore, 56%. The ash content was very small (0.04-0.05%).

C. J. WEST

**Technical utilization of chlorine for the digestion of plant fibers.** P. WAENTIG. *Papierfabr., Heft- u. Auslandheft* 1922, 67-71.—Review of patent and periodical literature.

C. J. WEST

**Chemical preparation and treatment of films.** S. HALEN. *Kunststoffe* 12, 73-6 (1922).—Discussion of patent literature, covering the use of nitrocellulose,  $\text{CuO-NH}_4\text{OH}$  cellulose, acetylcellulose, viscose, cellulose hydrate in alk. soln., and other products.

C. J. WEST

**Preparation of straw pulp, specially for straw board.** F. HOYER. *Papierfabr.* 20, 653-8, 689-93, 729-34 (1922).—A good, general review of the manuf. of straw pulp.

C. J. W.

**Sulfate pulp production. Odors and rational operation.** WILLI SCHACHT. *Papierfabr., Fest- u. Auslandheft* 1922, 71-9.—The sources of odors in the sulfate or straw pulp mill are enumerated. Patented processes by S. are illustrated by means of which recovery in the sulfate process can be carried out without the disagreeable odors which are so objectionable in the ordinary sulfate mill.

C. J. WEST

**Occurrence of thiosulfate and polythionate in sulfite liquors.** RUDOLF SIEBER. *Zellstoff u. Papier* 2, 51-3, 106-14 (1922).—Sulfite liquors, prepd. from gases free of sublimed S, contain only  $\text{SO}_2$  and  $\text{SO}_3$  with possibly a trace of thiosulfate. Mention is made of the possibility of lower oxidation products of S being formed during the prepn. of sulfite liquors by various methods and the effect of  $\text{As}_2\text{O}_3$  and  $\text{SeO}_2$  is discussed. Definite proof of the positive action of As or Se in the formation of these lower oxidation compds. was not obtained. It was shown that the cause of the formation of polythionate was the sublimed S. The amt. of polythionate and thiosulfate found was very small, however, and did not represent the total amt. of sublimed S which was present in the S burner gases. A portion of the thionates appears quickly to decompose into  $\text{SO}_2$  and the actual amt. of thionates in equilibrium with the sulfite liquor seems to be very small. Methods for the analysis of these compds. are given. C. J. W.

**Acid and alkaline bleaching.** HOTTENROTH. *Wochbl. Papierfabr.* 52, 3784-9 (1921); *Zellstoff u. Papier* 2, 6-10 (1922).—With equal consumption of Cl, the same bleaching action is not obtained with a cold, as with a warm, acid bleach liquor. In the presence of  $\text{CO}_2$  there is an increase in the Cu no., though the whiteness of the pulp is not so pronounced as when an alk. bleach is used. The result corresponds to that obtained with an equal acidity of  $\text{H}_2\text{SO}_4$ . To obtain the best results with  $\text{CO}_2$ , sufficient acid should be used so that the bleaching action remains effective as long as possible. Better results are obtained by a combination of acid and alk. bleach, than by either one alone. Alk. followed by acid bleach does not give the results that the reverse order does. The best practice is to consume  $\frac{1}{3}$  to  $\frac{1}{4}$  of the Cl in an acid bath and the remainder in an alk. bath.

C. J. WEST

**Raw materials for paper-making.** ANON. *World's Paper Trade Rev.* 77, 1596, 1598 (1922).—The exptl. stage as regards paper-making qualities of bamboo, waste raw cotton and papyrus is past. A summary of claims made for each is given.

C. J. WEST

**Paper-making in Siam.** ANON. *World's Paper Trade Rev.* 77, 1418, 1420(1922).—Among suitable materials available in Siam are *Bambusa arundinacea*, *B. polymorpha*, *Cephalostachyum pergracile*, and *Brousonetia papyrifera*. C. J. WEST

**Coloring of paper.** H. DIRRDORF. *Papierfabr., Fest- u. Auslandsheft* 1922, 52-55; cf. *C. A.* 16, 2223.—A discussion of the dyes to produce definite colors on paper and also of the dyes for special kinds of papers and for special methods of dyeing. In the soln. of basic dyes it is advantageous to add about 2 g. of 30% AcOH per l. of H<sub>2</sub>O to counteract the hardness of the H<sub>2</sub>O. C. J. WEST

**Dyeing of paper pulp.** EMIL HEUSER. *Papierfabr.* 20, 549-55(1922); *Paper Trade J.* 74, No. 26, 44-5(June 29, 1922).—A lecture, largely historical. The effect of the sizing, the character of the water, the effect of fillers and the simultaneous weighing and coloring of paper are also discussed. The use of Al, Ca and Mg silicates and the corresponding lakes is briefly mentioned. C. J. WEST

**China clay.** ANON. *World's Paper Trade Rev.* 77, 1494(1922).—Use of china clay in newsprint is rapidly increasing. Three classes are known to the trade, coated art, imitation art and supercalendered. In coated art, base paper is coated with china clay, then rolled and burnished; it has a smooth face for half-tone printing. Imitation art is completely finished on a special paper-making machine, while the supercalendered is calendered and then coated and rolled. C. J. WEST

**Calculation of the efficiency of drying machines.** F. STRAUCH. *Papierfabr., Fest- u. Auslandsheft* 1922, 56-66.—Extensive calcs. are made of the influences which det. the steam consumption per kg. of paper. The results are shown in tables and curves. They will form a valuable basis for further work on the practical study of the drying end of a paper machine. C. J. WEST

**How Paper is Made. Essential Steps in the Manufacture of Paper from the Time it is a Raw Product.** Kalamazoo, Mich.: Bermingham and Presser Co. 31 pp.

**Bibliography of Periodical Publications on Paper-making and Allied Subjects during 1920.** 40 pp. 5s. **During 1921.** 47 pp. 5s. Tech. Sect. of Papermakers' Assoc. of Gt. Britain and Ireland.

**Proceedings of the Technical Section, 1921.** Vol. 1, parts 1 and 2. 188 pp. 15s. 6d. Vol. 2, part 1. 118 pp. 10s. 6d. Papermakers' Assoc. of Gt. Britain and Ireland.

**Papermaking Materials.** Compiled by Clarence J. West. Cambridge, Mass.: Arthur D. Little, Inc. Reviewed in *Svensk Pappers Tid.* 24, 218(1921).

## 24—EXPLOSIVES AND EXPLOSIONS

CHARLES E. MUNROE

**Estimation of the nitro group in aromatic organic compounds.** II. T. CALLAN AND J. A. RUSSELL HENDERSON. *J. Soc. Chem. Ind.* 41, 157T-61T(1922).—The Knecht-Hibbert method (*C. A.* 14, 2264) is greatly improved by standardizing the TiCl<sub>3</sub> with recrystd. *p*-nitroaniline and, when TiSO<sub>4</sub> is used, boiling in an atm. of CO<sub>2</sub>, as proposed by English (*C. A.* 14, 3794); a reflux condenser is used to prevent loss of volatile nitro compds., and a 5% soln is employed. Tables of data are given for analyses of  $\alpha$ -nitronaphthalene with various titanous solns., of mononitro hydrocarbons, nitro-monochloro compds., substituted nitrochloro compds., nitrophenols and nitrocarboxylic acids under a great variety of conditions such as in NaOH, or alc. solns., reflux or no reflux, min. and large excess HCl, quiet and vigorous boiling and the like. This method is of value in the dyestuff as well as the explosives industry.

CHARLES E. MUNROE

**The lead plate test as applied to detonators.** BENNETT GROTTA. *Chem. Met. Eng.* 26, 1126-32 (1922).—The app. for and the method of making the test are described. The appearance of the Pb plate after the detonator has been fired upon it furnishes a pictorial representation of the explosive action of the detonator charge. In the center at the point of contact with base of the detonator there occurs a depression which is dependent for depth both upon the size and quality of the detonator. Radiating from this central depression, or perforation, are numerous striations of fine dotted lines which constitute the real index to the quality of the detonator and the explosive effect of its compn. Each dotted line is the result of a glancing blow inflicted by a single particle of the detonator shell. The detonation of  $\text{Hg}(\text{ONC})_2$  of good quality bursts the casing into a multitude of concentric rings, each of which is, in turn, shattered into numerous small fragments. As the quality of the detonator is lowered the action of the explosive charge is less brusque, the shell fragments become larger, and radial striations on the lead plate tend to be replaced by large pittings or splotches at irregular intervals on the face of the lead plate; these are caused by the larger fragments. If, because of prolonged exposure to moisture, a defective grade of fulminate, or a faulty mixt., the detonator becomes practically worthless as an initiator it will merely rupture the casing into a small number of broad strips. Consequently this detonator will produce a few broad, ribbon-like impressions on the lead plate radiating from an almost imperceptible depression where the base of the detonator was in contact with it while striations and pittings will be absent. A set of plates is shown by means of which detonators can be classified and selected for the particular work desired. Excellent illustrations are given showing the extent of shell fragmentation, the app. for making lead plate tests, the Munroe effect from indentation of dynamite cartridges or detonators and the effects of various mixts. of  $\text{Hg}(\text{ONC})_2$  and  $\text{KClO}_3$ . Data are given of tests of detonators on a mixt. of TNT 92% and  $\text{Fe}_2\text{O}_3$  8% and also on dynamites of various degrees of sensitiveness. The fragmentation tests were made by firing the detonators in a bomb filled with common salt; the fragments were recovered by dissolving out the salt.

CHARLES E. MUNROE

**Trauzl's method of determining power of explosives by lead cylinders.** DOMENICO LODATI. *Giorn. chim. ind. applicata* 4, 90-1 (1921).—By the use of spheres instead of cylinders, more correct results are obtained. ROBERT S. POSMONTIER

**Apparatus for determining stability of nitrocellulose and smokeless powder.** J. D. BERKHOUT. *Z. ges. Schiess-Sprengstoffw.* 17, 33-4 (1922).—Stability is detd. by heating samples in closed weighing bottles at 95°, 105° or 110°, noting loss of wt. in a definite period, as well as time required for evolution of red fumes. A special app. devised for maintaining const. and uniform temp. consists of a cylindrical copper air bath with glycerol-filled jacket, heated by a ring gas burner equipped with oil-Hg regulator. The bath has a double-walled cover filled with mineral wool, and an opening for a thermometer. It is covered with asbestos and the entire app. is surrounded by a covered cylindrical sheet-metal screen to reduce heat loss. The bottles are placed on a perforated shelf 2.5 cm. above the bottom of the bath. A registering thermometer is also provided for making a permanent record of temp. during a test. A second type of bath is equipped with a motor-driven device for agitating the air, by means of which a variation of not more than 0.5° is maintained throughout the bath.

C. G. STORM

**A method of testing the degree of incorporation of explosives and other powders.** E. P. PERMAN. *J. Soc. Chem. Ind.* 41, 155T-7T (1922).—It appears that explosives such as mixts. of TNT with  $\text{NH}_4\text{NO}_3$  are now being made for use as blasting explosives by mixing them in edge-runner mills as has been the practice in the manuf. of gunpowder and as in the latter case it is found that the degree of incorporation is dependent on the

size of the charge, the r.p.m. of the wheels and time of exposure of the charge on the bed of the mill to the action of the wheels. These factors will vary for each type and size of mill and the kind and fineness of the components. As a certain intimacy of the mixing is sought it has been the custom in the manuf. of gunpowder to det. when this point has been reached by taking samples from the mill and noting the residue left on "flashing." As it is not feasible to apply a flashing test to TNT mixts., P. has devised a rapid method for analyzing small samples (of approx. one mg. in wt.) by nesslerizing them in a Duboscq. colorimeter. The technic developed is described in detail and data are given showing the accuracy of the method and the results of its application in studying the influence of time, wt. of charge and the speed of milling on the rate of incorporation.

CHARLES E. MUNROE

**The manufacture of ammonium nitrate.** E. M. SYMMES. *Chem. Met. Eng.* 26, 1069-1074(1922).—A description of modern operating practice, with considerations affecting the design and operation of  $\text{NH}_3$  stills, scrubbers, condensers, neutralizing tubs, evaporators and crystallizing kettles, and discussions of the effect of impurities in the  $\text{NH}_3$  and the  $\text{HNO}_3$  on the yields, closing with a brief account of the use of  $\text{NH}_4\text{NO}_3$  in explosives.

CHARLES E. MUNROE

**Fire hazards in chemical plants.** ANON. *Chem. Age* (N. Y.) 30, 181-2(1922).—This is a statistical study by the National Fire Protection Assoc. of fire losses in chemical plants with a review of the circumstances in the case of some typical fires. The information collected for 473 fires is classified as to causes, whether common or special, and it appears that about 71% of them were due to hazards incident to the chem. industry. The instances especially reviewed indicate that the application of reason and forethought would have prevented most of them from occurring.

C. E. M.

**Pyrofulmin, a conversion product of mercury fulminate.** A. LANGHANS. *Z. ges. Schiess-Sprengstoffw.* 17, 9-11, 18-21, 26-8(1922).—The insensitive, non-explosive product resulting from the long heating of  $\text{Hg}(\text{ONC})_2$  at temps. up to  $100^\circ$  was investigated. The explosive strength plainly decreased after 30 hrs. heating at  $90^\circ$ ; after 50-60 hrs. the rate of change rapidly increased; after 90-100 hrs. the product was inert and non-combustible. A similar result was obtained in 160 hrs. at  $80^\circ$ . L. designates the product as "pyrofulmin." It is insol. in  $\text{H}_2\text{O}$  and the usual org. solvents, is neutral to litmus, evolves gas and deposits Hg on igniting, but does not char; it is not detonated by  $\text{Hg}(\text{ONC})_2$ . Analysis gives approx. Hg 76.5, N 9.7, C 6.2, O 7.5%, indicating loss of C and O from the original fulminate. The behavior of pyrofulmin with various reagents was investigated. On heating to various temps. up to  $180^\circ$  decompn. of the pyrofulmin continued, being greatly accelerated at  $160^\circ$  and above. The evolution of gas from  $\text{Hg}(\text{ONC})_2$  at temps. as low as  $85-90^\circ$  was noted but no analysis was made of the gas. Tests of fulminate compns. in blasting caps and primers showed that the fulminate became inert on long heating at  $90^\circ$ , the mixts. thereby becoming insensitive. It is suggested that the conversion of  $\text{Hg}(\text{ONC})_2$  into a non-explosive material by heating offers a convenient means of rendering primers and detonators in loaded ammunition inert for safety in salvage operations.

C. G. S.

**Present practice of dynamite and chemically pure glycerol distillation.** J. W. BODMAN. *J. Ind. Eng. Chem.* 14, 487-91(1922).—This system utilizes the double effect, or heat regenerator principle used in multiple evapn. by injecting the vapor from evapg. weak glycerol water (sweetwater) into the still and by superheating this vapor with the hot glycerol vapor from the still. The equipment and technic as described effect marked economies in steam and power consumption, give highest yields by eliminating loss of glycerol in handling and evapg. large quantities of sweetwater, give max. recovery in the form of high gravity dynamite or c. p. glycerol in a single distn. and

greatly economize floor space by including evaporator and concentrator units as part of the distn. system under the same vacuum system. CHARLES E. MUNROE

**Studies on the nitrotoluenes. VIII. Binary systems of *m*-nitrotoluene with another mononitrotoluenes.** J. M. BELL AND J. L. McEWEN. *J. Ind. Eng. Chem.* 14, 536-8(1922); cf. *C. A.* 15, 1814.—This paper contains the data and curves for the binary systems of *m*-nitrotoluene with *o*- and with *p*-nitrotoluenes. In the binary system of *m*- with *p*-nitrotoluene the conditions are simple, there being two curves meeting in a eutectic point. Gibson, Duckham and Fairbairns' diagram of 3 curves (*C. A.* 16, 1506) is believed to result from the fact that their *f.-p.* detns. are too low. In the binary system of *m*- with *o*-nitrotoluene 2 curves on the *o*-nitrotoluene side represent the stable and metastable forms, the curve for the latter beginning at  $-10.37^{\circ}$  and descending roughly parallel to the stable form. If it were possible for this to reach the lower eutectic it would probably be found about  $-30^{\circ}$ , corresponding to about 46% of *m*-nitrotoluene. CHARLES E. MUNROE

**Burning of 200,000 pounds of picric acid at Sparta, Wisconsin.** C. E. MUNROE. *J. Ind. Eng. Chem.* 14, 552-4(1922).—This material, stored in bbls. contg. 500 lbs. each, burned away in 30 min. without explosion because of its being stored in the open-shed type of magazine. The fire communicated to the contents of a second magazine contg. over 217,000 lbs. of picric acid but this fire was extinguished without material loss. CHARLES E. MUNROE

**The velocity of combustion of colloidal powders.** PAUL BOURGOIN. *Compt. rend.* 174, 532-4(1922).—The discordance between interior ballistic formulas and the results of actual trials is due to the fact that the expression adopted for the velocity of combustion contains no factor for the temp. of the medium in which the combustion is effected. This error is demonstrated by expts. in bombs in which mixts. of a rapidly burning with a more slowly burning or of coated and uncoated powder are exploded, or as another variant the given charge is in one trial exploded in a vacant bomb and in another trial in a bomb partly filled with Cu gauze. From exptl. data B. formulates the law of the combustion of colloidal powders as follows: "The velocity of combustion of a colloidal powder is at each instant proportional to the quantity of heat (supposed to be uniformly distributed) contained in the unit vol. of the cavity in which the combustion of the powder has been effected." CHARLES E. MUNROE

**Additions, removals and changes in permissible list of explosives from March 31 to May 31, inclusive, 1922.** S. P. HOWELL. *Bur. of Mines, Repts. of Investigations* No. 2362, 2 pp.(1922).—Five additions, 11 withdrawals and 6 changes are noted. Information is given for the explosives added to the permissible list on class designation, vol. of poisonous gases evolved, characteristic ingredient, grade of detonator to be used in firing it, wt. of  $1\frac{1}{4} \times 8$  in. cartridge, smallest permissible diam. of cartridge, unit defective charge, rate of detonation of  $1\frac{1}{4}$  in. diam. cartridge and manufacturers. CHARLES E. MUNROE

**The background of detonation.** S. W. SPARROW. National Advisory Committee for Aeronautics, *Technical Notes* No. 93, 17 pp.(1922).—This is a contribution to the study of the phenomena in internal-combustion engines. It especially deals with the effect of the temp. and pressure of the charge before combustion in the belief that careful study of this "background" can throw considerable light on results that have been obtained in the investigation of detonation at the Bureau of Standards and elsewhere. It is shown that compression and explosion pressures, scavenging and operation of the ignition system all play a prominent part in the phenomena of detonation. Pre-ignition and detonation are conceded to be entirely independent phenomena, and it is shown that overheating troubles are more likely to be from pre-ignition than from detonation. Calcd. explosion pressures show a probable increase

of over 25% for a scavenged, in comparison with an unscavenged, engine having a compression ratio of 4. An influence which vitally affects detonation is the ignition timing or spark advance. The max. explosion pressure should occur when the pressure prior to combustion is greatest. Since, in the engine, the charge is compressed most at the top center the max. explosion pressure should result from a spark so timed as to cause the actual combustion to take place at that part of the stroke.

C. F. M.

**The explosion of two cars of ammonium nitrate at the Aktiengesellschaft Lignos Explosive Factory at Kriewald, O. S. D. W. BRAMKAMP. *Z. ges. Schiess-Sprengstoffw.* 17, 67-8(1922).**—Two cars of  $\text{NH}_4\text{NO}_3$  being unloaded at the factory where  $\text{NH}_4\text{NO}_3$  explosives were manufd. exploded, completely wrecking the factory and killing 19 persons. A crater 20 m. wide and 6-7 m. deep was produced. Blasting with explosive charges was being resorted to in order to break up the hard caked mass of  $\text{NH}_4\text{NO}_3$ . Analysis of samples from other cars of the same shipment showed  $\text{NH}_4\text{NO}_3$  99.3%,  $\text{H}_2\text{O}$  0.3%, ash 0.16%,  $\text{SO}_2$  0.3%, other impurities traces. Tests with this material showed it to be insensitive to the effect of the explosion of 2 No. 8 detonators imbedded in a sample of 100 g. Complete detonation of a 200-g. sample resulted, however, from the explosion of a priming charge of 47 g.  $\text{NH}_4\text{NO}_3$  mixed with 2 g. TNT, the priming charge being fired with a No. 8 detonator. The explosion shattered the base portion of a 15 cm. steel shell, with 15 mm. walls, in which the beaker contg. the charge was placed, even though the charge was entirely unconfined. Attention is called to the danger of the practice known to exist in certain chemical and fertilizer factories, of blasting hard masses of  $\text{NH}_4\text{NO}_3$ .

C. G. STORM

**The passage of flame through perforated plates and through tubes of small diameter. MINERS' LAMPS COMMITTEE. *Memorandum No. 4*, Mines Department, London, 19 pp.(1921).**—A modern development in the construction of miners' safety lamps is the use of perforated plates instead of gauzes. The idea is not novel for it dates from Davy's researches. The fact that in recent years there has been considerable improvement in the art of perforating metals no doubt accounts for the resuscitation of the idea and its practical application. The investigation of the flame of the most explosive mixt. of  $\text{CH}_4$  and air through perforated brass plates dealt with (a) the diam. of the holes, (b) the thickness of the plate, (c) the no. of holes or open area per unit of plate area and (d) the effect of continued burning of fire-damp. The specifications for perforated metal, to serve as protection for the air-inlet holes of bottom-feed lamps, that combine security with general utility, are thickness, not less than  $1/16$  in.; open area not greater than 0.55 in., and diam of perforation, not greater than 0.8 in. In connection with the investigation of the passage of flame through tubes of small diameter there is given an interesting literature review while there are recorded the data of tests with tubes of various diams. in various positions and it is concluded "that it should be possible to construct a bottom-feed safety-lamp in which the air is fed to the flame through tubes of 3 mm. diam. not less than 2 cm. in length; and that, if longer tubes are employed, say, 6 cm. in length, they can safely be of larger diam. up to 4 mm. Such tubes would themselves afford protection against the passage of the flame of an explosion from within the lamp without the necessity for either gauzes or perforated plates, if used for the air-inlet to the lamp."

CHARLES E. MUNROE

**The passage of the flame of an explosion from within miners' lamps fitted with chimneys. MINERS' LAMPS COMMITTEE. *Memorandum No. 5*, Mines Department, London, 12 pp.(1921).**—The substitution of a chimney for the inner gauze of a miner's lamp facilitates the passage of the flame of an internal explosion of fire-damp and air through the outer gauze. This disability attaching to the use of a chimney was well known to the inventor of the Mueseler chimney, who accorded rigid dimensional limits to his device but many chimneys employed in other lamps differ widely in these dimen-

sions and some perform very different functions. This record embodies the results of investigations of the effects of chimneys, caps and gauzes of different designs and arrangements and the conclusion is reached that all lamps fitted with a chimney and single outer-gauze, except such as are designed to supply air solely below the wick, should be required to pass a test similar in character to that described in this memorandum, the means employed to render the lamp capable of passing such a test being left to each designer, who may choose between proportioning the chimney and outer gauze in accordance with the principles therein set forth or of providing a gauze cap to the outer gauze or a metal cap perforated, or unperforated to the chimney.

CHARLES E. MUNROE

**Liquid-air explosives in the Lorraine iron mines.** CH. BENOIST. *La Nature* 1922, 260-264.—In a well written and beautifully illustrated article the methods of liquefying the air and prepg., placing and firing of the shots are described. Although the liquid air is subject to large loss from evapn. the cost of blasting was less than with any other explosives. Its use has now been restricted by a tariff imposed on the cartridges.

CHARLES E. MUNROE

**The passage of the flame of an explosion through wire gauze.** MINERS' LAMPS COMMITTEE. *Memorandum No. 1*, Home Office, London, 16 pp.(1920).—This report deals with the passage of the flame of an explosion through standard mesh gauze, and the propagation of flame in mixts. of  $\text{CH}_4$  and air. The tests were made with standard single and double gauzes at atm. temp. and at  $200^\circ$ , this last temp. being  $20-30^\circ$  higher than the max. attained by the crown of the gauze of a miner's lamp after long continued burning in actual use in pure air, and it was found that before a lighted miner's safety lamp fitted with a single gauze becomes incapable of resisting the passage *outwards* of the flame of the most explosive mixt. of  $\text{CH}_4$  and air, with which the lamp is presumed to be suddenly and completely filled, it must be fitted with a glass nearly 15 cm. long, thus confirming the results of expts. in 1912, *viz.*, that such a flame does not pass through to the outside atm. when the distance from the point of ignition to the single gauze disk is 5 cm. or less but does pass through when the distance is 7.5 cm. or more and can ignite an explosive mixt. beyond. With the double gauze disk these distances are, resp., 23 and 30 cm. The majority of miners' lamps have glasses not over 6 cm. in length, so that, when fitted with a single gauze of standard mesh and wire, they can easily resist the passage of flame due to explosions of fire-damp and air within them. This memorandum contains an extended historical review, discusses mathematically the "safety numbers" for thickness of wires and sizes of apertures in gauzes, and gives results of investigations made looking to increasing the ventilation and illuminating powers of safety lamps.

CHARLES E. MUNROE

**Report on the use of celluloid in the construction of miners' electric lamps.** MINERS' LAMPS COMMITTEE. *Memorandum No. 2*, Mines Department, London, 6 pp.(1921).—The celluloid cases of accumulators of safety lamps having on several occasions been set on fire by a short-circuit while the lamp was in use, underground investigations were made to devise means for guarding against (1) the ignited celluloid causing an ignition of fire-damp external to the lamp, (2) the evolution of fumes dangerous to the health of the miner and (3) the development of a pressure sufficient to burst the lamp. The results are given *in extenso*, together with a detailed account of a lamp explosion, and the Committee recommends that for electric safety lamps which are or may be nearly gas-tight and in which accumulators with inflammable cases are used, the case of the lamp should be provided above the level of the accumulator with not less than 5 vent holes of not more than  $1/16$  in. diam.

CHARLES E. MUNROE

**Safety in the use of explosives in the presence of fire damp.** ETHENNE AUDIBERT. *Rev. ind. minérale* No. 32, 181-206(1922).—From a mathematical and exptl. study of the ignition of fire-damp when firing explosives it is concluded that the cause of this

ignition of the surrounding gaseous medium is the heat created by compression of this surrounding gas. It was found, furthermore, that by using a suitable solid packing or stuffing, a very violent explosive could be detonated without causing ignition of the  $\text{CH}_4$ .

C. C. DAVIS

## 25—DYES AND TEXTILE CHEMISTRY

L. A. OLNEY

**New method of colorimetric analysis (for dyestuffs).** PAUL DOSNE. *Bull. soc. ind. Mulhouse* 88, 73-7(1922).—Sealed note No. 2100, deposited July 2, 1911. For each colored soln. there is a definite and critical concn. for which the characteristic absorption spectrum is sharp and complete; for lower concns. some of the lines are not visible and for higher concns. the lines are too broad and blend into one another. D. described a simple all-glass app. by means of which the thickness of the layer of soln. which is observed through the spectroscope can be readily changed so as to get a sharp and complete spectrum. The thickness of this layer (in cm.) multiplied by the concn. (in cg. per l.) is called the *sp. index of coloration*. The app. is specially suited to Formanek and Grandkouglin's method of spectroscopic analysis.

A. P.-C.

**A hyposulfite solution for dye analysis.** EDOUARD SIFFERLEN. *Bull. soc. ind. Mulhouse* 88, 80(1922).—Weakly acid ( $\text{AcOH}$ ) hyposulfite soln. contg. Na citrate is not decomposed when boiled, but is rapidly oxidized. By adding  $\text{CH}_3\text{CHO}$ , it can be kept several days without oxidation in an atm. of  $\text{CO}_2$ . It does not reduce safranin in the cold but reduces azo dyes quant. in boiling soln. The following method of prepn. is given: Dissolve separately 5 g. of concd. hyposulfite (Badische) in 250 cc. of water contg. 10 g. of  $\text{NaHCO}_3$  and 25 g. of Na citrate in 250 cc. of water to which are added 5 cc.  $\text{CH}_3\text{CHO}$  in 10 cc. of alc. Mix the 2 solns., remove the excess of  $\text{CH}_3\text{CHO}$  by passing a current of  $\text{CO}_2$  and dil. to 1 l. (Cf. following abstract.)

A. P.-C.

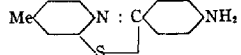
**Comments on Sifferlen's hyposulfite solution.** MARCEL BADER. *Bull. soc. ind. Mulhouse* 88, 80-3(1922); cf. preceding abstract.—Aq.  $\text{Na}_2\text{S}_2\text{O}_4$  solns., even when protected from the action of oxidizing agents, decompose according to the equation  $2\text{Na}_2\text{S}_2\text{O}_4 + \text{H}_2\text{O} \rightarrow 2\text{NaHSO}_3 + \text{Na}_2\text{SO}_3 + \text{S}$ . The reaction is accelerated by the H ions which are continually being formed. The Na citrate decreases the H-ion concn., thereby stabilizing the soln. The  $\text{CH}_3\text{CHO}$  combines with the hyposulfite to form acetaldehyde-Na bisulfite and acetaldehyde-Na sulfoxylate, which are rather less stable than the corresponding  $\text{CH}_3\text{O}$  compds. At temps. of 80-100° they are hydrolyzed sufficiently rapidly for analytical purposes. The soln. loses its reducing power in 5 days, as compared with 3 days for Siegmund's soln. (acetone-Na hyposulfite). J. Béha and M. Hueber obtained concordant results with this soln. on various azo and benzidine dyes.

A. P.-C.

**Note on the use of sodium tungstate lakes for coloring aniline black by the Prud'homme process.** CHARLES SUNDER. *Bull. soc. ind. Mulhouse* 88, 78-9(1922).—The lakes pptd. on Na tungstate are 2-5 times more concd. than those pptd. on tannin. They are more resistant to the action of alkalis, and they can give half-tones by superposition. For lighter lakes, by pptg. the lake on a  $\text{ZnO}$  suspension a brighter color is obtained than by mixing the concd. lake with  $\text{ZnO}$  after pptn.

A. P.-C.

**Colors derived from dehydrothio-*p*-toluidine and the two primulines, and their affinity for cotton.** G. R. LEVI. *Giorn. chim. ind. applicata* 4, 62-3(1921).—Dehydrothio-*p*-toluidine (D)



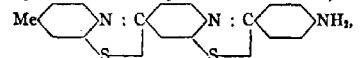
was prepd. by boiling *p*-toluidine

under a reflux with deficiency of S (20% less than theoretical) until  $\text{H}_2\text{S}$  ceased to form.



The mass was treated with HCl to eliminate the excess of *p*-toluidine, then washed with 2% NaOH and finally with H<sub>2</sub>O. Recrystd. twice from alc., it m. 188-9°. The

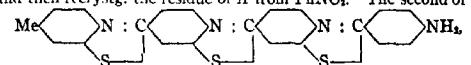
1st primuline base,



(A) was obtained

from the mixt. of *D* and *A* prepd. by heating a mixt. of 100 parts *p*-toluidine and 65 parts S to 220-30°. *D* was first extd. from the mixt. by treating repeatedly with amyl alc. and then recrystg. the residue of *A* from PhNO<sub>2</sub>. The second or Kalle's primuline

base,



(B) was prepd.

by heating a mixt. of *D* and S in almost theoretical proportions (the S 5% in deficiency) at 300° to cessation of liberation of H<sub>2</sub>S and extg. the mass with EtOH to eliminate traces of *D*. *D* dissolves easily in 40% H<sub>2</sub>SO<sub>4</sub>, diazotizes well and quant. with *N* NaNO<sub>2</sub> at about 8-10° (by addn. of ice). The copulation of this diazo compd. with H acid is normal and can be carried out in carbonate soln. *A* dissolves in H<sub>2</sub>SO<sub>4</sub> with some difficulty, but the diazotization is equally quant. The copulation is also normal. *B* dissolves with great difficulty in 40% H<sub>2</sub>SO<sub>4</sub> and could not be diazotized quant. The degree of affinity of the coloring substances from bases *D*, *A* and *B* for cotton is the same for all (if solns. of equal color are taken), and the mother liquors resulting after dyeing have equal colors. This is due to the fact that the brilliancy of color of the bases diminishes in proportion to the increase in the number of the thiazole groups.

ROBERT S. POSMONTIER

**Dyeing of direct blacks on cotton piece goods.** RAFFAELE SANSONE. *Am. Dyestuff Rep.* 10, 402, 422-5(1922).—The applications of direct blacks are many and often cover fields where the S colors are valueless or have so far found little use. The dyes are employed for (1) jet blacks, (2) grays of different shades and fastness, (3) ground for aniline black, (4) compound shades, (5) half wool or half silk goods, (6) covering in calico printing, (7) ground to be discharged in calico printing. Among these uses the S colors have replaced direct blacks only in the case of fast jet blacks. A suggested plant for the production of jet blacks with substantive colors is described and the advantage of the machine method are indicated.

L. W. RIGGS

**The after-chroming of wool.** A. A. CLAFLIN. *Am. Dyestuff Rep.* 10, 397-400 (1922).—In many cases, particularly for the after-chroming process or for wool printing, it is necessary to use a Cr salt such as the acetate, chloride, fluoride, nitrate, oxalate, or sulfate in order to avoid the oxidizing action of the dichromates. These salts were used in amts. contg. equiv. wts. of Cr in tests with alizarine Yellow GO, Acid Anthracene Red 3B, Chloramine (Diamine) Fast Red F, Carmoisine Conc., Acid Anthracene Brown FW, Acid Alizarine Blue SKV, Acid Violet 6RN, and Acid Alizarine Green CG Extra. Each test was made on 10-g. skeins of worsted yarn, and the results of the acid dyeing, effects of the dichromate and of each of the six Cr salts above named are given. Each test was followed by scouring tests. In the main all of the Cr salts change the shade less from that obtained in the simple acid dye than does the dichromate. The shades obtained with the various salts resemble each other more than they do those obtained with dichromate. With Carmoisine Brown FW and Violet 6RN the oxidizing action of dichromate is apparently essential to develop the shade.

L. W. RIGGS

**Chrome colors on cotton hanks.** R. K. SHETH. *Indian Text. J.; Am. Dyestuff Rep.* 10, 428-9(1922).—Details for dyeing chrome yellow, orange and green are given. The orange is made by washing the chrome-yellow yarn with clear water, passing it through dild. boiling lime water, soaping and drying. Chrome green is obtained by topping light indigo blue with chrome yellow.

L. W. RIGGS

**Construction, dyeing and finishing of homespun.** G. E. TEMPLETON. *Am. Dyestuff Rep.* 10, 401-2(1922).—Directions for weaving, bleaching, dyeing, scouring, milling, fulling and finishing are given. L. W. RIGGS

**Recent development of the scouring and bleaching of cotton. A review of the literature for the years 1920, 1921.** LILLIAN B. STORMS. *J. Home Econ.* 14, 212-9 (1922). L. D. ELLIOTT

**The evaluation of unscoured wool.** E. JACOB. *Industries du cuir* 1922, 148-50.—The sample of wool is weighed, then sorted by sieving into 3 parts, the bulk, dirty matter (defiled with dung and urine), and impurities (earth and sand), which are weighed separately. The difference between the wt. of these 3 and that of the sample is returned as loss in screening. The bulk and the dirty matter are then analyzed separately for water, grease, foreign matter, and wool. Numerical examples are given.

F. L. SEYMOUR-JONES

**Laundrying.** LYDIA JACOBSON. *J. Home Econ.* 14, 109-13(1922).—A discussion of recent investigations on laundrying soaps and bluiings. HELEN N. ELLIOTT

**Modern methods of removing spots.** ERNST MICHAELIS. *Deut. Färber-Ztg.* 58, 475-6(1922).—Spots are classified in 2 principal groups according as they are removed by water or not. Those not removed by water are subdivided into 9 groups on the basis of their chem. compn. or of the means used for their removal. The technic employed for the removal of spots belonging to each group is described with much detail. Before applying the various spot-removing treatments, the goods including the spots themselves must be thoroughly cleaned and brushed. L. W. RIGGS

**New principle for weaving.** WILHELM OSTWALD. *Umschau* 26, 321-3(1922).—The methods of obtaining different shades by weaving variously colored threads in different proportions are described. L. W. RIGGS

**Faults in the manufacture of wool-fattening and spinning oils (WELWART) 27.**  
**Dyeing of paper pulp (HEUSER) 23.** Composition of oil and rubber (for waterproofing textiles) U. S. pat. 1,417,103, 26.

GEORGEVICS, G.: *Kurzgefasstes Lehrbuch der Farbenchemie.* Leipzig: Franz Deuticke. 219 pp. Reviewed in *Textilber. wiss. Ind. u. Handel* 2, 320(1921).

**Dye.** F. KUNERT. Can. 219,405, June 6, 1922. A dye in solid or paste form consists of a mixt. of alkali salts of nitrosamines and alkali salts of arylamides of 2,3-hydroxynaphthoic acid.

**Dyeing.** F. KUNERT. Can. 219,406, June 6, 1922. In the one-bath method of dyeing the fiber impregnated with a soln. of the dye of the preceding pat. is passed through a feeble acid or acid salt.

**Weighting silk to be dyed black.** A. W. SCHMID. U. S. 1,417,206, May 23. Silk which is to be dyed black is first weighted according to the usual tin-phosphate process and is afterward treated with a boiling lather or froth bath of a hematein soln. to which chrysalides boiled in H<sub>2</sub>O have been added.

**Dyeing.** P. ONNERTZ. Can. 219,752, June 20, 1922. A neutral or feebly alk. soln. of 1,4-diamino-2-chlorobenzene in the presence of an oxidizing agent is used for dyeing fur.

## 26—PAINTS, VARNISHES AND RESINS

A. H. SABIN

**Graphic analysis of sublimed white lead.** BURTON PAXTON. *Chem. Met. Eng.* 26, 989(1922).—For rapid analysis of sublimed white lead, det. ZnO and total Pb volumetri-

cally, and then by means of the chart given, interpolate the corresponding percentages of  $\text{PbSO}_4$  and  $\text{PbO}$ . F. A. WERTZ

**China wood oil—its test for purity.** E. W. FASIG. *Paint, Oil and Chem. Rev.* 73, No. 21, 11-12(1922).—Review. F. A. WERTZ

**The effect of the solvent on the character of lacquer films.** HANS WOLFF. *Farben-Ztg.* 27, 2086-7(1922).—The volatile thinners in a lacquer do not act merely as solvents, but often have an effect on the character of the film produced. The initial drying or setting of the film will be influenced by the concn. at which gel formation takes place, and this is often dependent on the degree of dispersion of the resin or other non-volatile constituent of the lacquer. Changes in degree of dispersion may take place with changes in concn. If high dispersion exists a large proportion of the volatile thinner may evaporate before gel formation takes place, so that little volatile matter will be retained in the film; and if low dispersion exists, then the gel will form more quickly and will retain large amounts of volatile thinner, so that there is appreciable contraction on final drying and the latter film is more likely to crack. The degree of dispersion is often influenced by the addition of small quantities of other constituents, and for this reason certain mixed solvents may produce better films. The "blooming" of films produced from solms. of certain resins in alc., and their failure to do so when amyl alc. is used, may be due to differences in the dispersion of the resins in these mediums.

F. A. WERTZ  
**Manufacture of satin white.** P. O. SCRIBE. *Oil, Paint and Chem. Rev.* 73, No. 22, 10-11(1922).—See C. A. 14, 3801; 15, 3401. F. A. WERTZ

**New white pigments.** C. A. KLEIN. *J. Soc. Chem. Ind.* 41, 209-10R(1922).—Ti and Sb oxides are finding some use as paint pigments; the latter is being manufactured in Australia by direct roasting of the coarsely crushed ore. F. A. WERTZ

**The production of ultramarine.** HANS HADERT. *Farben-Ztg.* 27, 2154-5(1922).—A review of raw materials and processes used in the manufacture of ultramarine blue and green. F. A. WERTZ

**Volumetric determination of lead peroxide in minium.** A. BONIS. *Ann. fals.* 15, 157-9(1922).—The drawbacks of Topf's modification of Diehl's method for the detection of  $\text{PbO}_2$  (treating with KI in  $\text{AcOH}$  soln. in the presence of a large excess of alk. acetate to keep  $\text{PbI}_2$  in soln., and titrating the liberated I with  $\text{Na}_2\text{S}_2\text{O}_3$ ) as usually carried out are: loss of I, and frequent formation of a ppt. of  $\text{PbI}_2$  which is very difficult to dissolve. The following procedure is advised. (A) Dil. 24.4 g. of 40° Bé.  $\text{HNO}_3$  to 100 cc. (B) Cold satd. soln. of  $\text{AcONa}$ . (C) 12% soln. of KI in B. Weigh out 0.5 g. of sample in a small glass or porcelain dish, add 2.5 cc. of A and break up any lumps. Transfer to a 200-cc. Erlenmeyer flask by means of 25 cc. of B, shake, add 10 cc. of C, and titrate the liberated I with 0.1 N  $\text{Na}_2\text{S}_2\text{O}_3$ . If there is enough Fe to interfere with the end point, add an excess of  $\text{Na}_2\text{S}_2\text{O}_3$ , make up to 100 cc. with B, filter, and titrate the excess of  $\text{Na}_2\text{S}_2\text{O}_3$  in an aliquot. A. P.-C.

**Alcohol varnishes.** B. WALTHER. *Chem. Tech. Wochschr.* 5, 379-80(1921); *Chimie et industrie* 7, 964(1922).—A discussion of the advantages of alc. as a varnish solvent and of the choice of gums to use, showing that coumarone resins, rosin, and other brittle resins should not be used, and that best results are obtained with synthetic resins. A description is given of a standard method of mfg. alc. varnishes for various purposes. A. P.-C.

**Examination of floor polish and other preparations containing turpentine. Tests for purity of oil of turpentine.** J. PRITZKER AND ROB. JUNGKUNZ. *Schweiz. Chem. Ztg.* 1922, 203-7, 219-23, 231-4.—Floor polishes containing turpentine were exposed in open vessels for protracted time periods. In every case the  $n_D$  of turpentine isolated from such preps. showed slight increases over the  $n_D$  of the component turpentine

before exposure. Turpentine may be isolated from floor polishes by steam distn. without carrying with it more than traces of the solid components originally present in the polish. A no. of methods for testing turpentine are critically examd., and the method of Eibner and Hue (*C. A.* 4, 3134) is recommended with slight modifications, which materially cut down the time required for the test. The turpentine (10 cc.) (after isolation by steam distn.) is *very gradually* run into 15 cc. of  $H_2SO_4$  (d. 1.84) contained in a "*turpentine-oil tester*" (a modified Babcock bottle) and the mixt. is cooled and agitated, and subsequently centrifuged for 5 mins. (800-1000 revolutions per min.). The clear residue is measured and is termed the "Eibner-Hue no." (E-H no.). The E-H no. should not exceed 1.5 cc., and the refraction of the residue measured in the Zeiss butyrorrefractometer should not be under 105. Steam-distd. untreated turpentine showed a refraction (butyrorrefractometer) of 69-75. The E-H no. coupled with the refraction before and after  $H_2SO_4$  treatment gives a definite index of the purity of the turpentine.

L. E. WISE

**Manufacture of typewriter ribbons and carbon paper.** PAUL J. HASSETT. *Am. Dyestuff Rep.* 10, 403-4 (1922).—The ribbon is very closely woven 36 to 40 in. wide from long staple Sea Island or Egyptian cotton and finished by removing wax, oil, size or anything that may hinder the absorption of ink. Bleaching is unnecessary. The cloth is slit into strips of the required ribbon width and the edges are sealed with an adhesive, usually made of glue and glycerol, to prevent fraying. Ribbon inks are a combination of colors ground in oil, with or without the addition of sol. colors. The dry colors are ground for several days in steel roller mills to produce the necessary fineness. Black record ink is lampblack in oil toned up with oil-sol. blacks such as nigrosine and induline bases. Purple ink is usually made by pptg. methyl violet on a base of  $Al(OH)_3$  and  $BaSO_4$  and this lake is ground in a non-drying oil with the base of methyl or crystal violet dissolved in oleic acid. Blue ink is made from Victoria Blue B base dissolved in oleic acid and combined with a blue lake ground in oil. Red is usually made from Lithol or Geranium Lakes ground in oil. Copying inks are made by grinding water-sol. colors in non-drying oils, the latter acting only as a vehicle. Carbon-paper inks are mixts. of wax, color and oil. The same colors may be used for ribbons, and the wax employed is generally carnauba. For black paper carbon blacks made from natural gas are used. At present in America ribbons and papers are made principally from domestic materials and a considerable export trade is carried on. L. W. RIGGS

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Determination of the particle size of pigments ((Vogt) Luttringer) 30.

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LEHNER, SIGMUND: *Chemiker u. Fabrikant Die Tinten-Fabrikation*. 7th Revised ed. Vienna and Leipzig: A. Hartleben. 224 pp. M 36.

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Gold-colored sulfides and vermillions of antimony. P. CHAILLAUX. U. S. 1,417,033, May 23. Natural Sb sulfide is melted in a closed vessel and air is passed through it while regulating the temp. in accordance with the particular color (golden or crimson) desired.

Plant for producing yellow or other pigments. JNO. MACFARLANE. Can. 218,371, May 9, 1922. The app. specified is for producing a pigment from waste pickling acid liquor.

Composition of oil and rubber. J. I. O'BANION. U. S. 1,417,103, May 23. Lined oil 50 gals. and rubber 7 lbs. are boiled together for 4 hrs. and after cooling are mixed with benzine 5 gals. and liquid drier 5 gals. to form a compn. suitable for water-proofing textile fabrics or leather substitutes.

**Waterproofing composition.** G. W. MAGNUS. U. S. 1,416,852, May 23. A mixt. adapted for waterproofing fabrics, cement or metals is formed from raw linseed oil 40, rubber 1, Pb acetate 1.33 parts and sufficient gasoline to thin the mixt.

## 27—FATS, FATTY OILS AND SOAPS

R. SCHEPUEL

**Annual review in the domain of fats, oils and waxes for 1920.** W. HERBIG. Z. *deut. Oel-Fett-Ind.* **41**, 353-5, 386-8, 403-4, 417-9, 435-7, 450-2, 481-3, 500-2, 515, 538, 555, 574-5, 603-4, 650-3, 666-8, 683-4, 697-9, 713-5, 730-2, 752-3, 768-70, 790-2, 811-3, 830-2, 853-5(1921); **42**, 7-8, 39-40, 76-7, 98-9, 137-8, 153-4, 185-6, 201-3, 233-5, 249-50, 267-8, 283-4(1922).—A critical annual review under the following captions: A. Physical properties. B. Chem. behavior. C. Analysis. D. Investigations of old and new vegetable oils and fats. E. Animal fats and fish oils. F. Special analytical and scientific examns. of fats and oils. G. 1. Technical operations and uses of fats, oils and waxes. 2. Refining. 3. Cleavage. 4. Soap manuf. 5. Special products. 6. Apparatus.

P. ESCHER

**Bleaching of oils and fats.** A. E. COHEN. *Seifensieder-Ztg.* **49**, 340-2(1922).—Dried and acid-free sesame oil was bleached for 15 min. under regulated but varying conditions, with 5 different bleaching agents: bone black, fullers earth, norite, blood charcoal and Florida earth. The influence of temp. and time is small. Below 100° air does not injure bleaching. The presence of H<sub>2</sub>O increases the bleaching action and facilitates filtration. Certain combinations of diff. bleaching agents increase the bleaching action but never increase it beyond the effect of bleaching successively with the partial amts. contained in the mixt. The article is illustrated by 5 graphs. P. E.

**New process for hydrogenation of organic compounds, especially of fats and oils.** FERDINANDO ULZER. *Giorn. chim. ind. applicata* **3**, 464-5(1921).—U. used as *catalyzer* a double silicate of Mg and Ni, obtained by a pptn. method. The products obtained were beautifully white, without a previous bleaching of the oil or fat.

ROBERT S. POSMONTIER

**The glycerides. X. The glycerides of goose fat.** A. BÖMER AND H. MERTEN. Z. *Nahr. Genussm.* **43**, 101-37(1922); cf. C. A. **15**, 183.—Purified goose fat had an I value of 66.2, m. 36.7° and sapon. value of 196.8. Only three fatty acids were found: stearic acid 3.8, palmitic acid 21.2 and oleic acid 72.3%. The margaric acid reported in this fat by Klimont and Mayer (cf. *Monatsh.* **36**, 281-7(1917)) was probably a eutectic mixt. of palmitic and stearic acids. Five glycerides were found: (a) Palmito-distearin, m. 63.5°, 63.4° (in very small amt.), (b) steardipalmitin, m. 57.8°, 3-4%, (c) dioleostearin about 5%, (d) dioleopalmitin about 30% and (e) triolein about 45%. There appeared to be one other glyceride present with one mol. of oleic acid and two mols. of satd. fatty acids.

D. B. DILL

**The refining of palm oil for edible purposes.** M. F. LAURO AND W. H. DICKHART. *Am. J. Pharm.* **94**, 245-9(1922).—Palm oil was refined for edible use by first refining with lye as is done with cottonseed and other edible oils, then bleached and deodorized. When the acid content was above 15% the loss of oil and the mechanical difficulties involved were too great to permit refining on a wholesale scale. An 18% acid oil gave a refining loss of about 50%. On the other hand 12% acid oil had a refining loss of less than a quarter of the total oil treated. The crude oil contained moisture 2.04, impurities (dirt, etc.) 1.27, unsapon. fatty matter 0.64, free fatty acids (as oleic) 11.73%,  $d_{15}^{20}$  0.8556, I no. (Wijs) 54.3, sapon. no. 198.5,  $n_D^{20}$  1.4628, titer of the fatty acids 45.1, I no. of the fatty acids 52.1, neutralization no. of fatty acids 200.1. Refined

oil contained free fatty acids (as oleic) 0.10%,  $d_{15.5}^{20}$  0.8592, I no. (Wijs) 53.5, sapon. no. 196.3,  $n_D^{30}$  1.4627. The crude oil was refined with 13.5% of 18° B $\phi$ . NaOH with a loss of 23.5% of the oil. The color and appearance of the refined oil were like those of the grade known as Red Sherbro. Its taste was sweetish and not unpleasant, but with a distinct palm-oil after-taste. The characteristic odor, that of violets, still persisted. The soapstock from the refining process was thoroughly mixed and analyzed. Its color was a dirty orange-yellow, and its consistency hard and compact. No free alkali was present. The soap made by purifying the stock was of excellent appearance and grain, hard, lathered well and possessed good detergent properties; it contained water 27.58, total fatty matter as fatty acids 62.23, free oil 24.95, total alkali as Na<sub>2</sub>O 3.10, glycerol 2.20, impurities 5.30%, titer of fatty acids 44.8, I no. of the fatty acids 52.5, neutralization no. of the fatty acids 199.7. The refined, bleached and deodorized oil had  $d_{15.5}^{20}$  0.8596, I no. 53.2, sapon. no. 196.0,  $n_D^{30}$  0.14634, m. 40.8° (capillary method), Halphen test for cottonseed oil negative, Villavecchia test for sesame oil negative.

W. G. GAESSLER

**Electrolytic extraction of cod-liver oil.** ANON. *Chemist and Druggist* 95, 568 (1921).—A demonstration in Bergen (Norway) of the Rogers-Bennet System. A sketch of the app. and a description of the process are given (cf. C. A. 14, 855). S. W.

**The application of Villavecchia's test to olive oils.** JEAN PRAX. *Ann. fals.* 15, 159-61 (1922); cf. C. A. 15, 3911.—The red coloration frequently given by pure olive oil with Villavecchia's reagent is due to a coloring matter which is pressed out of the pulp of the fruit and is sol. in the oil. Treatment with ammoniacal alc. removes or changes this constituent so that it does not react with Villavecchia's reagent; this is due to the action of the NH<sub>3</sub>, not the alc.

A. P.-C.

**Identification of Turkey red oils.** N. WELWART. *Seife* 44, 84 (1921); *Chimie et industrie* 7, 960 (1922).—Sulfonated castor oil is generally neutralized with NaOH or with Na<sub>2</sub>CO<sub>3</sub>, giving 2 different kinds of oil. Blends of these oils are used in cotton dyeing, and NH<sub>4</sub>Cl is added. NH<sub>3</sub> is detected by means of Nessler's reagent. For distinguishing between oils neutralized with NaOH and with Na<sub>2</sub>CO<sub>3</sub>, evap. 5 cc. of a 20% soln. of the oil. A film of characteristic appearance is formed, according to the nature of the oil.

A. P.-C.

**Faults in the manufacture of wool-fattening and spinning oils.** N. WELWART. *Seifensieder-Ztg.* 49, 307, 329 (1922).—I. Faults in manuf.: (a) Preps. which are poor in fat contain mainly filling material such as karragheen infusions, mixed with fatty acids, fatty oils and Na<sub>2</sub>CO<sub>3</sub>. (b) Preps. rich in fat but effecting little fattening contain too much soap and too little free fat or oil, and have a ratio from 1:1 to 3:1 of saponified fatty acids to free fat. (c) Lack of permanency when emulsified is due to too much or too little soap or the soap may contain fatty acids of too high a m. p., or an improper ratio of soap to fatty acids to neutral fat. (d) Difficulty in dissolving is caused by too much soap or by soap of high melting acids. (e) Preps. contg. NH<sub>3</sub> soaps lose some of their NH<sub>3</sub> in warm storage and then possess little emulsifying power; the same holds true for preps. contg. alc. (f) Wool fattenings contg. vegetable pectoid substances decompose when insufficient or volatile preservatives have been used, causing fungi growth and formation of org. acids, which in turn decompose the soap and may cause bad odors and loss of viscosity. (g) Sticky preps. are caused by the presence of castor oil, its fatty acids or their sulfonation products. Preps. of insufficient binding power contain too much soap. (h) Difficulty in washing out the fat from fatted wools is due to the presence of much unsapon. oil (mineral oil, cholesterol) or to some drying oil which forms oxidation products on the fiber. (i) Preps. contg. free NaOH (up to 1%) destroy the fiber; a small amt. of Na<sub>2</sub>CO<sub>3</sub>, on the other hand, does not injure it. II. Faults in application. (1) The after-darkening in storage of white wool is

due to the use of discolored wool-fattening or to the use of drying oils which are subsequently oxidized on the fiber. The most suitable fats are coconut and palm-kernel oil, which may in part be replaced by light colored tallow or olein. (2) Fish oils should never be used for fattening because they produce a bad odor and, on account of their oxidation products, cannot be easily washed out; uneven dyeing frequently results therefrom. (3) Fattenings are sometimes required to increase the wt. of the fiber to cover spinning losses, and preps. which contain much  $H_2O$  should be avoided for that purpose. (4) Preps. contg. mineral oil require much soap and soda for their removal and may cause uneven dyeing. P. ESCHER

**The bleaching of oils in soap making.** *Parfumerie moderne* Jan. 1922, p. 2; *Industrie chimique* 9, 213(1922).—Oils are easily bleached by benzoyl peroxide, which, when heated slowly, gives off  $O$ . The oil is heated to  $120^\circ$  with 0.2–0.3% of  $(BzO)_2$ , until the evolution of gas has ceased. A. P.-C.

**The use of hexalin and methylhexalin in soap-making.** BERGO. *Seifensieder-Ztg.* 49, 361–2(1922).—B. recommends the use of these solvents for soft soaps (K soaps) and liquid soaps. As much as 20% methylhexalin produces soaps of very superior cleansing power. P. ESCHER

**A new method for determining free fat in soaps.** OSKAR HAGEN. *Seifensieder-Ztg.* 49, 359–61(1922).—Three modifications for detg. free fat in soaps by shaking their  $H_2O$  soln. with gasoline or ether are described. H.'s method consists in powdering the dried soap with the aid of enough ignited sand to form a crumbling mass and extg. in a modified Soxhlet app. with gasoline (b. below  $60^\circ$ ). The detn. can be finished in one day. (This method has been practiced in the U. S. for many years.—Abstr.) P. ESCHER

**Liquid soaps from coconut oil.** M. DONIGER. *Chem. Met. Eng.* 26, 1132–3 (1922).—Liquid soaps normally contain  $H_2O$ , glycerol, and the K soap of coconut oil. A 35 to 40% soln. of dry soap will remain clear and transparent above  $60^\circ F$ . indefinitely but usually glycerol or alc. is added to maintain transparency at a lower temp. E. SCHERUBEL

**The various kinds and names of montan wax in Galicia.** BADERMANN. *Seifensieder-Ztg.* 49, 369–70(1922).—The standard name for montan wax in Boryslaw is ozokerit, other names being fossil or montan wax, mineral fat, etc.; in the Moldau region it is called zietriszit and around the Caspian Sea naphthil, naphatil (= non-naphtha), etc. "Marble-wax" is found 100–200 m. below the surface; it shows marble-vein coloration, m.  $85$ – $100^\circ$  and yields 30–40% pure ceresin. "Hard" or "crackwax" ("Sprung-Wax") is dark, coarse-grained, m.  $75$ – $90^\circ$ , and when of fibrous structure is called "fiber-wax." Waxes below  $75^\circ m. p.$  may show all colors, but usually darken when air-exposed; "matka" or "blister-wax" belongs to this class. "Bagga" is dark, of strong odor and contains kaolin. "Kanderball" is dark and smeary, contg. earthy material. "Lep" is a kaolin-slate, satd. with wax. In the trade 5 grades are recognized, ranging in m. p. from  $85^\circ$  to  $68^\circ$  for the first three grades and from  $68^\circ$  to  $50^\circ$  for the 4th and 5th grade. P. ESCHER

#### Laundering (JACOBSON) 25.

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HIRST, GEO. H.: *Soaps. A Practical Manual of the Manufacture of Domestic, Toilet and Other Soaps*. 3rd Ed. revized and enlarged. London: Scott, Greenwood. 440 pp. 21s.

SIMMONS, W. H. and AINSWORTH, MITCHELL C.: *Edible Fats and Oils. Their*

**Composition, Manufacture and Analysis.** 2nd Revised edition. London: Scott, Greenwood. 200 pp. 10s 6d.

STADLINGER, HERMANN. *Seifen-Industrie-Kalender 1922*. Leipzig: Eisen-schmidt & Schulze. M 20. Reviewed in *Seifensieder-Zig.* 49, 191(1922).

THOMSEN, E. G.: *Soap-Making Manual*. A Practical Handbook on the Raw Materials, Their Manipulation, Analysis and Control in the Modern Soap Plant. New York: D. Van Nostrand Co. 243 pp. \$4. Reviewed in *J. Ind. Eng. Chem.* 14, 666(1922).

## 28—SUGAR, STARCH AND GUMS

F. W. ZERBAN

**Starch and glucose from maize.** II-III. JOSEPH BURTT-DAVY. *S. African J. Ind.* 5, 177-83, 215-22(1922); cf. *C. A.* 16, 2426.—A review of the uses and manuf. of *gluten feed, starch, dextrin, acetone, glucose and glycerol* from corn. S. W.

**Report on maltose products.** O. S. KEENER. *J. Assoc. Official Agr. Chem.* 5, 436(1922).—Pptn. with alc. is a more promising method for detg. dextrin in the presence of glucose and maltose than the use of maltase, which is difficult to obtain, or that of yeast, which has proved unsatisfactory. Further study of the alc. method is recommended.

F. W. ZERBAN

**Determining activity of invertase.** T. S. HARDING. *Sugar* 24, 89-90(1922).—A soln. of sucrose is prepd. so that 50 cc. soln. and 5 cc. water reads approx. 33.5° V. This soln. is of about 10% strength. Add to 50 cc. sucrose soln. 5 cc. invertase to be tested and hold at 30° for 10 min. The sucrose soln. should be made slightly acid with acetic acid to litmus paper. Stop the reaction and mutarotation by adding sodium carbonate just to alkalinity to litmus. Read in a 2 dm. tube. A decrease of 1.5° V. corresponds to 10% on a percentage basis. Invertase solns. showing a decrease of 15° V. are rated as 100%.

C. H. CHRISTMAN

**Relative sweetness of invert sugar.** J. W. SALE AND W. W. SKINNER. *J. Ind. Eng. Chem.* 14, 522-5(1922).—Invert sugar prepd. in soln. by the acid or by the invertase method, is contrary to accepted belief, 11% less sweet than the equiv. amt. of cane sugar. Sirups made with acid have a slightly harsh taste, while those made with invertase are smooth. When sirup prepd. with invertase is concd. by boiling at atm. pressure, color and candy flavor develop; boiling *in vacuo* produces little color and flavor. Sirup made with HCl was practically free from either, but had a slightly unpleasant taste. Directions for prepg. invert sugar sirups are given. F. W. ZERBAN

**The standardization of cane sirup.** I. H. MORSK. *Facts About Sugar* 14, 414-5, 419(1922).—Practical suggestions are given as to the means of obtaining uniformity of color and flavor. The two objects to be attained are first, the elimination of all impurities and second, the complete prevention of the formation of caramel. The accurate control of the clarification process is discussed as well as the special problems which are encountered, namely, the neutralization of H<sub>2</sub>SO<sub>4</sub>, the destruction of glucose, the darkening in color which occurs on standing, etc. Adoption of a definite final juice acidity is recommended in establishing a standard grade of sirup.

N. KOPELOFF

**Experiments on the distance of planting sugar cane.** WM. E. CROSS. *Louisiana Planter* 68, 348-9(1922).

C. H. CHRISTMAN

**The selection of a vegetable carbon.** W. H. DUNSTONE, JR. *Facts About Sugar* 14, 416-417(1922).—The factors to be considered as discussed are: decolorizing efficiency, filtering efficiency, size of grain, porosity of grains, color selection, proper facility of sweetening off, acid reaction, percentage of sol. salts, percentage of heavy



minerals, hardness of structure, compn. of structure, available supply, uniformity of quality, sp. gr., necessity or non-necessity of kieselguhr and presence of uncarbonized org. matter.

**The carbonatation process in Natal.** E. WUTHRICH. *Facts About Sugar* **14**, 460-461(1922).—The difficulties encountered are peculiar, because of the necessity for treating refractory cane juices of only one variety of sugar cane, namely Nba, which requires little water. Because of the presence of a large amt. of gummy matter, the use of the defecation process is attended by great difficulties and the sugar losses are unusually high. By the proper use of the carbonatation process the difficulties encountered were overcome. The advantages are enumerated as: (1) A beautiful white sugar (2) Seven % greater recovery of the sucrose in the juice. (3) An uninterrupted running of the factory, with removal of all the troubles in the filter-presses and other stations. (4) An increase in the capacity of the various stations of the factory, resulting also in a shorter season. The yield of sugar per cu. ft. of the various massecuites was considerably higher by the carbonatation process and the cost of production was very little more than that of mfg. defecation white sugar.

N. KOPELOFF

**Centrifugal pumps in sugar processes.** IRWIN McNIECE. *Sugar* **24**, 92-3(1922).—For the condenser system, sufficient capacity is necessary to provide water for condensation of steam. Bronze or brass linings are required where salt water is used. Capacity up to 9 million gal. per day is required. Sufficient capacity and high pressures on the discharge side must be provided for juices. The juice from the effects can be handled with ease if the pump is protected from foreign solids. C. H. CHRISTMAN

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**The solubility of crystallized strontium hydroxide (SIDERSKY) 2.**

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PICTET, JACQUES: *Sur les dextrines de polymerisation*. Genève: Imprimerie du commerce. 32 pp.

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**Corn starch.** A. W. H. LENDERS and P. W. ALLEN. U. S. 1,417,467, May 23. Residual protein impurities in corn starch are rendered sol. and dissolved by bacterial action and the starch is purified by sepn. from the sol. products, preparatory to conversion, evapn and crystn. of the conversion product.

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## 29—LEATHER AND GLUE

ALLEN ROGERS

**Animal hide as an amphoteric and colloidal protein.** W. A. RAKUSIN. Petrograd. *Kolloidchem. Beihefte* **15**, 103-84(1922).—A review of work on the mechanism and theory of the dyeing and tanning of hide substance, correlated with R.'s own recent work. The impossibility of consulting foreign literature since 1914 robs this paper of much of its value. Hide powder, unlike gelatin, contains traces of hydrolyzable S. In gelatin S is present as chondroitin-sulfuric acid. Hide substance contains carbohydrates extractable with 95% EtOH. Dyeing hide without mordants is a process simultaneously combining positive and negative adsorption. Hide is irreversibly dyed with acid and basic aniline dyestuffs without mordanting, except with crystal violet (reversible with 95% EtOH), methyl orange (reversible with boiling water), and methylene blue (reversible with both water and EtOH). This irreversibility supports the view of chem. combination between amphoteric protein and acid or basic dyestuff. Hide and proteins are not dyed by plant colors, such as litmus and turmeric. Tannin is positively adsorbed from soln. by hide, the process being reversible at ordinary temp. with water

and EtOH. Negative adsorption (adsorption of solvent) is practically nil, hence swelling in tan liquors is inappreciable. Protein color reactions on the hide before and after tannage show that tannin reacts only with the biuret-complex of the hide and not with the amino groups. The carbohydrate content of the hide diffuses into the tan liquors. With albumin tannin combines with all N groups except those of tyrosine. Adsorption expts. and the reversibility of tannage point to vegetable tanning being an adsorption, since stoichiometrical results are not obtained. The tendency of HCHO to form salts with amino acids shows that tannage with HCHO is a chemical combination. This is confirmed by the protein and carbohydrate reactions of HCHO-treated proteins. Aldoses, phenols, cresols, and thymol react chemically with proteins, all tanning hide except *o*- and *p*-cresol, taking the absence of the biuret reaction as a criterion of tannage. Picric acid and  $\alpha$ - (but not  $\beta$ -) naphthol also tan. Quinone tans, but acetone does not. The adsorption of Al salts by hide powder is irreversible and due to the combination of the protein with one of the hydrolytic products of the Al salt.  $(\text{AcO})_3\text{Al}$  soln. is an exception in that negative adsorption occurs. Fe tannage is of a similar nature. One bath Cr tannage is similar, but hide irreversibly adsorbs a max. of Cr at low concns. of Cr. [Data as to conditions of expts. are frequently lacking, rendering them inconclusive. No mention is made of H-ion concns., a knowledge of the work on which, published since 1914, explains most of the expts. described. ABSTR.]

F. L. SEYMOUR-JONES

**Leather chemical researches on proteins.** W. MOELLER. *Z. Leder- u. Gerberei-Chem.* 1, 188-203(1922).—In the prepn. of upper leather all proteins except the collagen of the hide are removed by fermentive action. In heavy leather these remain in the hide. Com. blood fibrin was taken as similar to the muscle protein, elastin, nerves, blood vessels, etc., of the skin, and the action of HCl, NaOH, gallotannin, quebracho, tannin, chrome alum, HCHO, and  $\text{Ca}(\text{OH})_2$  upon it studied. Fibrin was treated in 0.1, 0.5, and 1.0 N HCl for 8, 14, 21, and 28 days; it hydrolyzed from 3 to 12 per cent more readily than hide powder. With 0.01, 0.05, 0.1, and 1.0 N NaOH for the same times hydrolysis was very large, amounting to 100 per cent for the last two concns. With 2 per cent quebracho- and gallotannin solns., for 8, 14, and 28 days, the fibrin absorbed only traces of tannin and was hydrolyzed from 10 to 32 per cent. With acid and neutral chrome alum solns. (2 per cent  $\text{Cr}_2\text{O}_3$ ) for the same time periods, from 1.5 to 7 per cent of the Cr used was absorbed, while hydrolysis was only 2 to 3 per cent. With 2 per cent HCHO solns., from 0.7 to 2.9 per cent of HCHO was absorbed and hydrolysis was 1.3 to 2.3 per cent.  $\text{Ca}(\text{OH})_2$  of 0.01, 0.02, 0.04 N for 1, 8, 14, 21, and 28 days hydrolyzed from 3 to 20 per cent fibrin. The work demonstrates the importance of considering the effect of the preliminary network and the tannage on the non-collagenous proteins of the hide in relation to the qualities of the finished leather.

F. L. SEYMOUR-JONES

**The stability of different leathers to acids.** W. MOELLER. *Z. Leder- u. Gerberei-Chem.* 1, 217-24(1922).—Powd. samples of leather, tanned with quebracho, sulfited quebracho, and chestnut exts., were treated with 0.5 N  $\text{H}_2\text{SO}_4$ , HCl, and AcOH. HCl had the greatest destructive action, followed by  $\text{H}_2\text{SO}_4$ , while AcOH was minimal. Leather tanned with unsulfited quebracho was more readily attacked by AcOH than the other leathers; otherwise all 3 tannages showed approx. equal resistance. The use of  $\text{H}_2\text{SO}_4$  or HCl during tanning causes loss of hide substance, without any corresponding absorption of acid, up to a certain concn. AcOH used similarly does not hydrolyze the leather and renders it more resistant to hot water than acid-free leather.

F. L. S.-J.

**Durability of sole leather filled with cellulose sulfite extract.** R. C. BOWKER. *Hide & Leather*, Apr. 22, 1922, p. 13; *J. Am. Leather Chem. Assoc.* 17, 314-5(1922).—

As a filler for vegetable-tanned leather, sulfite cellulose ext. is as good as chestnut or quebracho exts.; it is as firmly fixed and yields as durable a leather. It has no deleterious effect during the aging of the leather.

J. A. WILSON

**The chemistry of salt stains and damages.** W. MOELLER. *Z. Leder- u. Gerberei-Chem.* 1, 210-7(1922); cf. *C. A.* 12, 2259.—Melanotic salt stains are due to the action of tyrosinase on the tyrosine-contg. proteins of the hide, e. g., muscle fibers, nerves, blood vessels, elastin, but not collagen. The tyrosinase reaction develops colors from red through brown and violet to black. Tests of  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$  in 0.01, 0.05, 0.1, 0.5, and 1.0 *N* concn. for 1, 2 and 4 weeks on hide powder showed only 1.0-3.9% hydrolysis. Satd. solns. of (a)  $\text{Na}_2\text{CO}_3$ , (b)  $\text{Na}_2\text{CO}_3 + \text{NaCl}$ , (c)  $\text{Na}_2\text{CO}_3 + \text{NaSO}_4$  acting for 2 and 4 weeks on hide powder and blood fibrin, showed only 0.5-2.5% hydrolysis. A salt-soda mixt. is recommended for salting hides. The salt represses bacterial activity and the soda hinders hydrolysis, including that of the tyrosine complex.

F. L. SEYMOUR-JONES

**The determination of moisture in leather—1922 committee report.** F. P. VIERCH, *et al.* *J. Am. Leather Chem. Assoc.* 17, 262-74(1922); cf. *C. A.* 16, 1029.—The difficulties encountered by analysts in trying to check each other in the detn. of moisture in leather were studied and discussed. It was concluded that unknown factors more influential than relative humidity affect the detn.

J. A. WILSON

**Determination of Epsom salt in leather—1922 committee report.** R. W. FRYE, *et al.* *J. Am. Leather Chem. Assoc.* 17, 274-84(1922); cf. *C. A.* 16, 355.—A single pptn. of  $\text{MgO}$  from the cold soln. by  $\text{NaNH}_4\text{PO}_4$  proved sufficient to give concordant results and this procedure is recommended.

J. A. WILSON

**Determination of oil and grease in leather—1922 committee report.** W. K. ALSOP, *et al.* *J. Am. Leather Chem. Assoc.* 17, 292-305(1922).—Chloroform exts. more matter from leather than does petroleum ether, and the difference is increased when the leather is wet. The committee is not in favor of substituting chloroform for petroleum ether as the official solvent.

J. A. WILSON

**Determination of glucose in leather—1922 committee report.** I. D. CLARKE, *et al.* *J. Am. Leather Chem. Assoc.* 17, 284-8(1922).—The results were inconclusive and it was recommended to continue the committee for another yr.

J. A. W.

**Analysis of chrome leather—1922 committee report.** L. BALDERSTON, *et al.* *J. Am. Leather Chem. Assoc.* 17, 289-92(1922).—A few comparative analyses of  $\text{Cr}_2\text{O}_3$  and  $\text{H}_2\text{SO}_4$  in chrome leather are given.

J. A. WILSON

**The methods of expressing the basicity of chrome liquors.** KARL SCHORLEMMER. *Collegium* 1920, 536-8.—Det. the  $\text{Cr}_2\text{O}_3$  content of green chrome liquor by oxidation with  $\text{H}_2\text{O}_2$  and  $\text{NaOH}$  and titration with  $\text{KI}$  and  $\text{Na}_2\text{S}_2\text{O}_4$  (cf. *C. A.* 12, 1426). Titrate hot a second portion of green chrome liquor with  $\text{NaOH}$ .  $\text{Cr}_2\text{O}_3$  calcd. from this detn. gives the amt. of  $\text{Cr}$  combined with the acid radical. The difference between this and total  $\text{Cr}_2\text{O}_3$  is the amt. of  $\text{Cr}$  combined with  $\text{OH}$  and is called the "basicity" of the liquor. By this method the basicity is the same whether the liquor contains chloride, sulfate, or a mixt. of the two and whether the chromium content is expressed as  $\text{Cr}_2\text{O}_3$  or  $\text{Cr}$ .

B. S. LEVINE

**Chrome tanning. IX. The relation between the properties of chrome liquors and the leather they produce.** Some notes on the mechanism of chrome tanning with bibliography. DONALD BURTON. *J. Soc. Leather Trades Chem.* 6, 157-80(1922); cf. *C. A.* 16, 1881.—A review and discussion.

J. A. WILSON

**Studies in chrome tanning. Equilibria between tetrachrome collagen and chrome liquors.** The formation of octachrome collagen. A. W. THOMAS AND MARGARET W. KELLY. *J. Ind. Eng. Chem.* 14, 621-3(1922).—When hide powder was kept in contact with a series of  $\text{Cr}$  liquors of increasing concn. for 48 hrs., a max. of 13.4 g. of

$\text{Cr}_2\text{O}_3$  was fixed by 100 g. protein, yielding tetrachrome leather. When a similar series was kept for 8.5 months, a max. of 26.6 g. was fixed, giving octachrome leather and indicating a combining wt. of 94 for collagen. Both max. occurred at a concn. of 15 g.  $\text{Cr}_2\text{O}_3$  per l. The formation of tetrachrome collagen was found not to be strictly reversible.

J. A. WILSON

**Comparative analysis of tanning materials—1922 committee report.** H. C. REED, *et al.* *J. Am. Leather Chem. Assoc.* 17, 256-62(1922).—Five samples of tanning materials were apportioned among 15 labs. for comparative analyses by the official method. The greatest differences between percentages of tannin found were from quebracho ext. 4.26, chestnut wood ext. 1.63, hemlock bark ext. 1.63, valonea beard 6.98, and mangrove bark 3.69.

J. A. WILSON

**The tanning process. II.** W. MOELLER. *Z. angew. Chem.* 35, 153-4, 160-3 (1922); cf. *C. A.* 15, 1086.—A discussion bringing out the following points: The modern theories of fiber structure (Zsigmondy's, Herzog's, etc.) are only modifications of Nägeli's micellar theory. A definite percentage of pelt is always dissolved by water (proteolytic factor) and the same amt. is dissolved from leather. This is partially decomposed hide substance and does not tan. A true tanning substance entirely prevents decompn. of the leather by hydrolysis or fermentation. By Fahrion's hot-water test vegetable-tanned leather is poorest and mineral- or quinone-tanned is best, but a detn. of the hide substance in soln. showed that all leathers gave up to water 9-10% of the hide substance present and all tannins are, therefore, about equal. As much as 50% of the hide substance may, however, dissolve from leather tanned with syntans and since the acid in syntans also hydrolyzes the hide substance, these are not true tannins. Fe salts do not tan because they dissociate too readily in soln. or in leather. Fe salts and syntans must be produced in an undissociable form before they will be satisfactory tannins. A tanning material must either contain a substance which is absolutely insol. in water or produce such a substance by combination with the hide. This substance must be peptized to the colloidal form. It can then form a protective coating on the fibers. In Fe or Cr tanning solns. alkali is the peptizer and the principal tanning material is free peptized metal hydroxides. Ordinary phenols can serve as peptizers for oil tanning.

I. D. C.

**Tannage of ostrich skins.** ANON. *Industries du cuir* 1922, 137-8.—Vegetable tanned ostrich skin resembles pigskin in texture, suppleness and color. It is from 1 to 1.5 mm. thick, and about 12 sq. ft. area. Small dark circular points and occasionally holes occur where large feathers have been removed. The leather has a mottled effect and is suitable for fancy upper leather.

F. L. SEYMOUR-JONES

**Cold soluble tanning extracts.** GABRIEL DESMURS. *Industries du cuir* 1922, 151-5.—Quebracho extd. direct from the wood is better than the dry ext., being less astringent owing to its higher non-tan content, and better colored, not having undergone oxidation. To solubilize  $\text{NaHSO}_3$  is added, together with some pyrogallol tan (sumac, chestnut, myrobalans) to lessen astringency and evoke acetic fermentation. The stems of tizrah (*Rhus pinnatifida*) have been developed in North Africa and Western Morocco as a source of tannin. It resembles quebracho in properties. Chem. bleaching of leather tanned with sulfited quebracho ext. is best replaced by treatment with weak acid sumac liquors.

F. L. SEYMOUR-JONES

**JETTMAR, JOSEF:** Das Färben des lohgaren Leders. 2nd Ed. revized. Leipzig: B. F. Voigt. M 40, bound M 50. Reviewed in *Collegium* 1922, No. 623, 62.

## 30—RUBBER AND ALLIED SUBSTANCES

JOHN B. TUTTLE

**Chemical and mechanical tests of rubber insulation.** A. VAN ROSSEM. *De Ingenieur* (Netherlands) May 28, 1921; *Elektrotechn. Z.* 43, 392-3(1922). An address. C. G. F.

**Methods for the analysis of rubber goods.** S. COLLIER, *et al.* *J. Ind. Eng. Chem.* 14, 560-4(1922).—Tentative methods of analysis are presented by a committee of the Rubber Division of the American Chem. Soc. for adoption as a standard procedure. The methods comprise: d., org. Me<sub>2</sub>CO ext., CHCl<sub>3</sub> ext., alc.-alk. ext., free S, total S, unsaponifiable compds., free C, total Sb, ash, S in the ash, Sb in the ash, BaSO<sub>4</sub>, glue and rubber hydrocarbon. C. C. DAVIS

**Use of bisulfite in sheet manufacture.** H. P. STEVENS. *Bull. Rubber Growers' Assoc.* 4, 228-9(1922).—The use of NaHSO<sub>3</sub> in the prepn. of sheet rubber is not generally advisable. Two samples of smoked sheet prepd. from latex to 1000 parts of which had been added 1 and 2 parts, resp., of NaHSO<sub>3</sub> cured more slowly than a control sample (ratio of times: 184:194:154). G. S. W.

**The hot vulcanization of rubber.** E. KINDSCHER. *Chem.-Ztg.* 46, 441-3(1922); cf. *C. A.* 15, 3227.—A general survey from the historical point of view of the theory and practice of hot vulcanization. C. C. DAVIS

**New process for the cold vulcanization of rubber.** G. BRUNI. *Atti accad. Lincei* [v] 30, i, 280-3; *Giorn. Chim. Ind. Appl.* 3, 196-7(1921).—Thiocarbamilide or other di-substituted aromatic thiocarbamide is formed in the mass of the material by the action of vaporized or dissolved CS<sub>2</sub> on an aromatic amine in presence of Zn or other oxide. J. C. S.

**Poisons in rubber nipples.** L. LUTZ. *Bull. sci. pharmacol.* 29, 121-3(1922).—L. found considerable Sb in rubber nipples sold on the market for nursing infants. The Sb was easily sol. in boiling H<sub>2</sub>O contg. a small amt. of NaHCO<sub>3</sub>. F. S. H.

**The composition of "golden antimony sulfide."** D. F. TWISS. *J. Soc. Chem. Ind.* 41, 171-2T(1922).—In view of the revival of interest in golden antimony sulfide (cf. *C. A.* 15, 486, 1469, 2596; 16, 661, 1681, 1886) attention is called to the important but evidently neglected work of Klenker (cf. *J. prakt. Chem.* 59, 150, 353(1899)). A review is given of his results, and it is maintained that his data show that the assumption of Short and Sharpe that "com. antimony sulfide contains no higher sulfide than tetrasulfide" and that "there is strong evidence of the existence of the latter" is premature and without justification. C. C. DAVIS

**Determination of the particle size of pigments.** W. W. VOGR. *India Rubber World* 66, 347-9(1922).—A turbidimetric method, professed to be more accurate than any previous method, is developed for detg. the av. size of the particles of pigments. It is recommended as a specification test for detg. the av. size of particles in different samples of the same pigment and for detg. the relative values of pigments in compounding. Suspensions of the pigment in liquid media are employed. The suspension is placed above a source of light with such a depth and of such a concn. that the rays are just shut off. This is detd. by extinction of the image of the filaments of a light. The obscuring power is assumed to be the total projected area of the suspended particles, and the results are calcd. in terms of the amt. of pigment necessary to extinguish the rays from a given area, or conversely the area which a given vol. of pigment will obscure. Assuming spherical particles, it is shown that obscuring power varies inversely as the diam. of the particles. The turbidimeter is a modified Nessler tube mounted above a parallel filament lamp, with devices for changing the level of the liquid, etc. Castor oil and glycerol are recommended for grinding media with EtOH and H<sub>2</sub>O, resp., as

suspending media. The reciprocal of the concn. in g. per l. divided by the height of the column in cm. gives the obscuring power in sq. cm. per g. Precautions are given for manipulation. The column should be 20-40 mm. when finally read. Results by various observers on a sample showed a max. deviation from the mean of 2%. The following values of the obscuring power of pigments in sq. cm. per cc. were obtained: gas black 11,000, Sb<sub>2</sub>S<sub>3</sub> 11,000, lampblack 8,000, Fe<sub>2</sub>O<sub>3</sub> 6400, ZnO 5650, lithopone 3600, corroded Pb 3100, sublimed Pb 2700, clay 2600, PbO 2400, MgO 1900, barytes 1500, asbestine 1400, Al 1520, CaCO<sub>3</sub> 1400, MgCO<sub>3</sub> 1100, tripoli 900, talc 760, mica 360.

C. C. DAVIS

**The determination of the size of the particles of pigments.** A. D. LUTTRINGER. *Caoutchouc & gutta-percha* 19, 11308-13(1922).—A résumé of methods recently developed for detg. the dimensions of the individual particles of pigments. These include the method of Wiegand (*C. A.* 14, 2732), of Green (*C. A.* 16, 841), of Vogt (preceding abstr.) and of Dinwiddie (under H. A. Gardner, *C. A.* 15, 605).

C. C. DAVIS

**Recent methods for the regeneration of old rubber.** S. HALEM. *Kunststoffe* 12, 57-8(1922).—Review of British, French and German patent literature.

C. J. W.

**Glue in rubber compounds.** A. B. KEMPEL. *Chem. Trade J.* 70, 452(1922).—The term "glue" is as comprehensive as "rubber," and conflicting exptl. results with glue are due to differences in the glues and to methods of mixing. It is impossible to mix carbon black uniformly into rubber without glue as a medium, but with glue, 68% of carbon black by wt. of the rubber has been mixed without detection by the microscope.

C. C. DAVIS

**Sodium silicofluoride as a mold preservative.** H. P. STEVENS. *Bull. Rubber Growers' Assoc.* 4, 227-8(1922).—Na<sub>2</sub>SiF<sub>6</sub> has some influence in preventing the growth of mold on smoked sheet in transit, but in the expts. quoted 0.1 g. per 100 cc. of latex did not entirely prevent the appearance of mold. The chemical in question is apparently without effect on the vulcanizing properties of the rubber. (Cf. *C. A.* 15, 3228.)

G. S. W.

**Rubber composition.** P. SCHIDROWITZ. *Can.* 219,488, June 6, 1922. A colloidal clay is impregnated with piperidine and sprayed with CS<sub>2</sub>; the product is incorporated with a rubber mixt. and the mass vulcanized.

**Vulcanizing rubber.** B. E. LORENTZ. U. S. 1,413,172, Apr. 18; *Can.* 219,474, June 6, 1922. Vulcanization is accelerated by the use of tetraalkylated thiuramdisulfide, e. g., tetramethylthiuramdisulfide 0.12%.

**Vulcanizing rubber.** D. F. TWISS. U. S. 1,413,813, Apr. 25. A soln. formed of caustic alkali and PhOH is used as an accelerator of vulcanization.

**Vulcanized rubber composition containing phenanthrene.** R. O. PHILLIPS. U. S. 1,413,557, Apr. 18. About 3-10% of phenanthrene is incorporated in rubber mixts. before vulcanization in order to replace wax in compns. for tires, elec. insulation or other purposes.

**Vulcanizers.** W. H. WELCH and H. FROST & Co., LTD. *Brit.* 175,036, Nov. 5, 1920. An electrically heated vulcanizer is provided with 2 or more heating elements, one of which maintains the app. at a steady temp., e. g., 175° F., and the other, or each of the other elements, a different temp., e. g., 300° F., means being provided to connect all the elements in the circuit to effect a rapid initial rise of temp. Two coils may be switched on at the beginning of the operation and one of them switched off when the desired temp. is reached. A suitable construction is specified.

**Repairing old rubber tires.** A. A. BAFFETTI. U. S. 1,412,992, Apr. 18. A mixt. contg. CCl<sub>4</sub>, linseed oil and a light hydrocarbon oil is applied to the tire and vulcanized for a short time followed by application of rubber cement and further vulcanization.

**Tire filling composition.** W. H. HAYWARD and ADANAC, LTD. Brit. 175,389, Nov. 12, 1920. In the manuf. of tire filling compns. consisting of oils treated with  $\text{SCl}_2$  and  $\text{MgO}$ , different kinds of oil are blended together so as to produce a mixt. having an I value of approx. 110. Soy bean, poppy-seed, or linseed oils may be mixed with rape, arachis, or olive oils; maize oil may be mixed with cottonseed oil or sesame oil, or both.

**Dental rubber.** T. A. SWARTZ and E. P. OTTMAYER. U. S. 1,413,071, Apr. 18. A vulcanizable material for making dental base plates of a color approx. that of the gums is formed of rubber, S and pigments such as lithopone and vermillion.

**Polymerized hydrocarbons (rubber-like product).** H. PLAUSON. U. S. 1,415,468, May 9. Hydrocarbons of the butadiene series are polymerized at temps. of about  $25-30^\circ$  under pressures of about 50-600 atm., in the presence of a diluent such as  $\text{N}_2$ ,  $\text{NH}_3$  or  $\text{C}_6\text{H}_6$ .

